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THE RECOVERY OF URANIUM FROM CARNOTITE ORES

Final Report

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June 30, 1949

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FINAL REPORT

on

THE RECOVERY OF URANIUM FROM CARNOTITE ORES

Contract No. AT-30-1-Gen-258

Prepared by: A. C. Richardson
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BATTELLE MEMORIAL INSTITUTE
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THE RECOVERY OF URANIUM FROM CARNOTITE ORES
(A. C. Richardson, Supervisor)

SUMMARY

The existing plants and processes used for treating western carnotite ores were developed to give the maximum recovery of vanadium. In order to establish the conditions required for maximum uranium recovery, research was conducted on the roasting and leaching of representative ores. The precipitation of the uranium from carbonate solutions, the effects of extraneous elements in salt roasting, and the effects of aging of calcines were also investigated. New methods of ore treatment were explored. Although the behavior of vanadium was not studied in this process, a few data are given which show the recovery of vanadium possible under the conditions favorable for the extraction of uranium. The results of the investigations may be briefly summarized as follows:

Each ore as mined presents an individual treatment problem for which specific conditions must be determined empirically. Generally speaking, the ores evaluated varied widely in composition and may be divided into three categories: (1) responsive, (2) mildly responsive, and (3) non-responsive to the salt-roast carbonate-leach treatment. From the responsive ores the extractions of uranium were from 80 to 90 per

cent and the less responsive ores gave extractions of from 34 to 60 per cent.

Roasting conditions were evaluated by small-scale batch tests and were substantiated by larger scale work with a continuous hearth roaster. Although roasting was not necessary for high uranium extractions by carbonate leaching, it was necessary for the simultaneous recovery of the vanadium. The optimum roasting temperature was not the same for the maximum recovery of both uranium and vanadium from any particular ore nor was it the same for the maximum recovery of uranium from both the fine and coarse portions of the same ore.

Under the proper conditions practically all(1) of the uranium in the raw ores was soluble in sodium carbonate. Roasting did not improve the solubility of the uranium in any of the ores tested but did improve the filterability and washability of the ore pulp. Roasting temperature was an important variable in obtaining optimum uranium extractions from individual ores while time, reagent additions, air flow, and particle size were of lesser importance.

By single additions of various compounds to uranium-bearing synthetic ores the effect of each element on the extraction of uranium and vanadium was determined. The beneficial effect of V_2O_5 was

(1) See Table 18 in the appendix, Raw Ore Leaching Test.

demonstrated on synthetic and natural ores, and the correct V_2O_5:U:CaO ratio(1) was determined.

With no free CaO present, a ratio of V_2O_5 to U of 5 to 1 in an ore was necessary for maximum solubilization of the uranium during roasting. The uranium is presumed to be soluble in sodium vanadate in that ratio, and free CaO has a deleterious effect on the extraction of both vanadium and uranium because of the formation of unreactive calcium vanadate. This reaction ties up the vanadium so that the available V_2O_5 to U ratio is lessened and the uranium extraction suffers in turn. The use of the proper ratio for each natural ore resulted in the following improvements: (1) higher maximum extractions of uranium from each ore, (2) similar roasting and leaching conditions for ores of different compositions, and (3) the possibility of blending ores prior to treatment.

The optimum amount of salt varied from 6 to 10 per cent. Pyrite in small amounts decreased the uranium extraction from any ore. However, when 16 per cent or more of pyrite was added, the resulting action aided the solubilization of the uranium, probably through the formation of soluble sulphates.

A decrease in the particle size from the standard minus 10-mesh roaster feed increased the uranium extractions from all ores tested but

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(1) The correct weight of V_2O_5 should equal 3 times the weight of free CaO plus 5 times the weight of the uranium.

also increased the problem of dust losses. A certain amount of air was necessary during roasting, and dry air proved better than air saturated with moisture.

Generally, the extraction of uranium with a sodium carbonate leach on raw ore could be improved somewhat, on all ores tested, by a low-temperature activation roast, principally because there was an increase in dissolution rate rather than an increase in soda solubility. The soda-soluble assay on the raw ores and ores roasted at 390 to 750°F. remained essentially the same.

Experimental work on leaching showed that the hotter the leach solution, up to the boiling point, the better the leaching results. Uranium solubilization in agitation leaching was rapid, being practically complete in 30 minutes. For maximum extraction the pulp density should be as dilute as practicable; the sodium carbonate concentration should be 9 per cent; and the particle size should be below 100 or 150 mesh.

While sodium bicarbonate aids in the dissolution of uranium, it is automatically present in sodium carbonate leaches of hot calcines. Some $NaHCO_3$ should be added for the maximum solubilization of uranium from a raw ore leach. Of other leaching reagents evaluated, only ammonium carbonate was as effective as the standard sodium carbonate leach.

The occurrence of an inflection point on the pH versus acid addition curve defines the complete precipitation of the sodium uranyl vanadate or yellow cake, from a pregnant sodium carbonate leach liquor

and should make it possible to control the precipitation by the use of pH determinations. Time, temperature, and CO_2 content of the solutions, as well as pH affect the completeness of the precipitation.

The loss in uranium extraction which occurred during the period, of time between discharge of roasted ore from the furnace and leaching, can be offset by a rapid cooling of the calcine. Rapid cooling is essential and may be accomplished by the immediate quenching of the calcine in the leach solution or by other means such as discharging the hot calcine on a cold steel plate. Appreciable aging losses were found to occur if the discharged calcines were allowed to cool for longer than 5 minutes. The shorter the cooling period and the more efficient the cooling action, the higher the final extraction and the lower the loss in uranium due to aging. In general, the faster the rate of heating, the higher the roasting temperatures required for optimum uranium extraction, and the less the effect of aging. The proper V_2O_5:U:CaO ratio produced a more stable non-aging calcine. With the exception of ammonium carbonate, none of the miscellaneous leaching agents tried were as effective as the standard sodium carbonate leach for the removal of uranium from aged calcines.

Roasting tests in the fluidized-bed furnace indicated that normal salt roasting of a carnotite ore may be performed in this type of equipment with air as a fluidizing medium. Dusting was not excessive, and the extractions of uranium were promising.

A cyclic leaching and precipitation system in which reagents might be recovered for re-use was investigated. Practically all of the vanadium could be recovered from the pregnant solution as ammonium metavanadate, after the removal of the uranium by pH adjustment.

RECOMMENDATIONS

Sufficient laboratory data have been obtained on the various carnotite ores to warrant recommendations as to the methods of handling these ores in order to obtain the optimum extraction of uranium by a salt-roast, sodium carbonate-leach process. Two separate methods of handling the salt-roasting treatment have been indicated by the experimental work. The methods are (1) roasting the ore as received and (2) adjusting the V_2O_5:U:CaO ratio prior to roasting. Because these methods differ radically, they are discussed separately in these recommendations.

Roasting of the Ores as Received

If the ores are to be sent as received to the roaster, it would be advisable to consider selective stockpiling of the ores on the basis of the treatment required to give the best recovery of uranium. Salt additions of from 8 to 10 per cent are beneficial to all ores and they need not be classified on that basis. With one or two exceptions

the use of pyrite was detrimental to uranium extraction and in general pyrite should be omitted.

Roasting temperatures, on the other hand, are important and may be used to advantage in segregating the ores. The optimum roasting temperature for the Garbutt Group ore is 1650°F. and it should be treated separately because this temperature will cause overroasting of the other ores tested in this investigation. The best roasting temperature for Wild Steer, Henry Mountain, and Ownbey ores is 1560°F. and they could be mixed in varying proportions without adversely affecting the uranium extraction to a serious extent. The Rico ore also can be roasted at this temperature.

The best uranium extractions from the Gyp Valley ore were obtained when it was roasted at 1420°F. without pyrite or at 1560°F. with 12 per cent of pyrite added to the charge. The low temperature or relatively large pyrite addition suggests that it should be treated separately from the other ores, since relatively low uranium extractions are obtained under the conditions that are optimum for the Wild Steer, and similar ores. A process other than that used at Monticello may be desirable for this ore.

The Bald Eagle ore has not proved amenable to the Monticello process and it does not appear advisable to attempt to treat it alone or with other ores by that method. For the present this ore should be

stockpiled by itself. Some preliminary laboratory tests indicate that this ore may be amenable to sodium carbonate leaching of the raw ore.

The effect of roasting time is less important than the effect of temperature but care should be taken to avoid overroasting. It is not advisable to roast the ores at the reaction temperature for more than 30 minutes.

In general the finer the particle size in the roaster feed the higher the uranium extraction from the calcine. For this reason the ore fed to the roaster should be as fine as commensurate with the values lost through dusting. For hearth roasters the best size probably will be minus 10 or 20 mesh. Because the most effective roasting is obtained on sizes finer than this, consideration should be given to other types of roasters such as fluidized-bed furnaces.

Adjusting the V_2O_5:U:CaO Ratio

In this method the natural or blended ores are adjusted, if necessary, by the addition of V_2O_5 to obtain the following ratio:

$$\text{Wt. \% of } V_2O_5 = \text{or} > 3.2 \text{ (Wt. \% CaO)} + 5 \text{ (Wt. \% U)}$$

Once this ratio has been obtained in the roaster feed it should be possible to operate at a standard roasting temperature of 1560°F. with a roasting time, at temperature, of 30 to 60 minutes. Under these conditions maximum uranium extraction should be obtained from all ores.

It may be advisable to pretreat the high-CaO ores by concentration methods to lower the CaO content prior to adjusting the V_2O_5:U:CaO ratio.

Quenching

Test work has indicated that if a calcine is cooled rapidly to approximately room temperature no appreciable loss in the uranium extraction results. Cooling slowly for as short a period as 15 minutes prior to leaching causes a serious loss in uranium extraction. Therefore, rapid quenching is essential in plant operation. Quenching either by rapid dry-cooling or directly in leaching solutions is effective. The addition of small amounts of V_2O_5 to the roast to correct the V_2O_5:U:CaO ratio, produced a more stable calcine and nullified these losses due to aging.

Leaching

The experimental work on the temperature of the leach solution showed that the hotter the solution the better the extraction. Leach solutions should be kept as close to the boiling point as is practicable. A large volume of leaching solution or a high-strength solution (up to 9 per cent of sodium carbonate) aids the extraction. Since excess carbonate must be neutralized, it is recommended that larger volumes at 3 per cent be used in preference to the smaller volumes of 9 per cent solution. The best extractions were obtained on materials ground to pass 150 mesh.

An agitation leach is recommended over a percolation leach because of increased efficiency in both leaching and subsequent washing operations. A countercurrent decantation and thickening process is possible. A leaching time of 30 minutes is required to give the maximum extraction with agitation leaching. If agitation leaching is continued for more than 24 hours the extraction drops, probably due to the conversion of the sodium carbonate to sodium hydroxide.

Precipitation

The Monticello precipitation process is efficient and generally satisfactory and is recommended for use. A closer control of the acid additions during precipitation can be achieved by pH control alone. A continuous recording automatic control of the titration is possible with an automatic shut-off at the points suitable for complete precipitation of yellow cake and red cake with no wasteful over-addition of acid.

INTRODUCTION

Carnotite and associated minerals occurring in sandstones in the Colorado Plateau area are a major source of uranium and vanadium in the United States. These deposits were exploited for radium as early as 1905, but were gradually abandoned when richer foreign sources were

developed. In recent years these deposits have been worked for their vanadium content, and during and since World War II, the ores have been treated for the recovery of both uranium and vanadium. The methods used in treating these ores, at the present time, were developed primarily for the recovery of vanadium. The recovery of uranium, being considered of secondary importance, has been relatively low. A commonly used flowsheet for recovering vanadium and uranium with a single leaching treatment is the salt-roast, carbonate-leach process such as that used at the Monticello, Utah plant prior to 1944.

When the Atomic Energy Commission made the decision to renew operations at several of the carnotite processing plants, with the primary objective of producing uranium, Battelle Memorial Institute was requested to investigate the salt-roast, carbonate-leach flowsheet, and study its suitability for the recovery of uranium from carnotite ores. A detailed study of vanadium and its behavior was not a primary objective of this project.

Objectives

The primary objective of this project was to evaluate and improve the salt-roast, carbonate-leach process for the treatment of low-grade carnotite ores, based on the flowsheet used at Monticello. Battelle was authorized to undertake this work on October 1, 1947, and the first representative samples of carnotite from Colorado were received on November 29, 1947.

The Monticello flowsheet and the evaluation of representative ores continued to receive major emphasis through August, 1948. The work was concentrated on obtaining operating data of immediate interest, particularly data that might modify the design of equipment or indicate major changes in the flowsheet prior to resuming plant operations at Monticello.

Since September 1, 1948, the research effort has been devoted to a second objective of exploring and developing, if possible, new and improved methods for the recovery of uranium from carnotite ores; checking and developing precipitation controls; and studying fundamentals such as the aging of calcines, the effect of associated elements in salt roasting, and leaching variables which effect the recovery of uranium.

This report summarizes the results of experimental work on "The Recovery of Uranium from Carnotite Ores". The information on which it is based has been submitted in monthly progress reports starting with that of November, 1947, and continuing through May, 1949. A list of all reports issued on this project is given as Table 15 in the appendix.

Prior Art

Carnotite and similar minerals are found most frequently as coatings or encrustations on sand grains. These uranium and vanadium minerals are soft, friable, and slime easily. In the past, mechanical means of concentration were employed using staged grinding, wet or dry.

The mineral-rich fines were then removed by dust collectors, gravity methods and/or magnetic or electrostatic separators. Recoveries were generally poor (50-60 per cent) and the grade of concentrate low.

To date, the process which has proven most economical for the recovery of vanadium, and incidentally uranium, has been the now universally employed chemical roast-leach process using salt (NaCl). The pre-roast treatment is practically the same for all variations of the roast-leach process and has been used for many years without much change or improvement. The ore is stage crushed, and dry ground to approximately 10-mesh size, mixed with up to 10 per cent of salt, and sometimes with added pyrite, and then roasted in a multiple-hearth furnace at about 1600°F.

The calcine from the furnace is quenched and leached with either water, dilute acid or 3 per cent sodium carbonate solution. The old Monticello process which was under investigation in the present work followed the sodium carbonate leach as is shown in Figure 18 in the Appendix. In this flowsheet the product from the roaster is quenched in a hot 3-per cent sodium carbonate solution, leached, and the soluble vanadium and uranium precipitated from the purified leach solution by the addition of sulphuric acid in a two-stage precipitation.

The pyrite is added to the furnace charge to fix the CaO as calcium sulphate and to offset the objectionable reaction of the CaO which is thought to form insoluble calcium vanadates during roasting.

In the course of the experimental work, several representative carnotite ores were evaluated to determine their amenability to the salt-roast carbonate-leach process for the extraction of uranium.

The ores investigated were representative of four types from the Colorado Plateau area: carnotite ores, roscoelite ores, a high-lime ore or calcareous shale, and a slime concentrate. The type, geographical source, and analyses of these ores are given in Table 16 in the Appendix. These ores would probably furnish a major part of the feed to custom mills such as the one at Monticello.

EXPERIMENTAL WORK

The subsequent sections of this report cover the following subjects: (1) small-scale tests to evaluate the response of individual ores to salt-roasting and carbonate-leaching, (2) the use of pH as a method for controlling precipitation, (3) the effect of associated elements on the extraction of uranium, (4) a study of the aging of calcines, (5) roasting in a fluidized bed, and (6) cyclic leaching and precipitation.

Evaluation of Individual Ores

A series of 15 individual ores and concentrates was evaluated from the standpoint of optimum salt-roasting and carbonate-leaching conditions.

Salt Roasting

The roasting variables studied included roasting, temperature, roasting time, reagent additions, airflow, and particle size of the roaster feed.

The standard procedure used in this evaluation consisted of roasting 100-gram charges of minus 10-mesh ore in a small electric tube furnace. The airflow during roasting was 0.12 c.f.m., the roasting temperature 1560°F., the roasting time 30 minutes and the sodium chloride addition equal to 10 per cent of the weight of the ore. In the small-scale tests, rabbling was omitted after it had been shown that it had no effect on the uranium extraction. In studying the effect of these roasting conditions, the variables were changed one at a time. The results were evaluated by determining the uranium extracted when the hot calcine was discharged into 400 cc. of a hot 3 per cent solution of sodium carbonate and agitated for 30 minutes.

Later, tests in a small-scale, single-hearth roaster using 5-pound samples substantiated the data obtained in the small tube furnace tests.

Roasting the ores failed to improve the uranium extraction over that which was obtained from leaching the raw ore. In some cases the soda-soluble uranium that could be extracted from unroasted ore was much greater than that extracted after normal salt roasting. However, low-

temperature roasting to 400°F. improved to a great degree the filterability and washability of ore pulps as compared with that of raw ore without lowering the extraction of uranium. Another effect of roasting the ores at low temperatures was that the rate of dissolution of uranium was increased. The soda-soluble uranium remained the same, but shorter leaching periods were necessary to accomplish the same extraction of uranium, probably due to the change in the character of the ore.

While roasting did not increase the uranium extraction, it was necessary for high vanadium extraction. Carbonate leaches on raw ores gave very low vanadium extractions (less than 20 per cent), but if the ores were given a salt roast at temperatures in the range of 1500 to 1650°F. from 60 to 90 per cent of the vanadium was extracted by the standard leaching procedure.

Effect of Roasting Temperature. The optimum salt-roasting temperature for maximum uranium recovery varied for each ore. The optimum temperatures for a number of ores are shown in Table 17 of the Appendix and may be summarized as follows: Gyp Valley, 1400°F; Wild Steer, 1540°F; Radium 7, 1560°F., and Garbutt, 1650°F.

The roscoelite Ore C-11 from Rico required roasting at 1560°F. for maximum uranium extraction.

Effect of Pyrite Additions. Pyrite added to the roast in amounts of 3 to 6 per cent definitely decreased the uranium extraction

from any ore. Amounts in excess of about 16 per cent, however, may increase appreciably the solubility of uranium . Because in other tests an SO_2 atmosphere in the furnace appeared to aid in the subsequent extraction of the uranium, it is assumed that a soluble uranium sulphate was formed in both cases.

Effect of CaO Content. Although Bald Eagle No. 1 ore was not responsive to the Monticello process, its high CaO content alone is not a criteria for judging its amenability. For example, Garbutt Ore C-9 was more responsive than Gyp Valley Ore C-8 even though it contained 3.8 per cent CaO as compared with 2.5 per cent in the latter. There seems to be no direct correlation between CaO assay and optimum roasting temperature for the different ores. The varied amenability cannot be related directly to the CaO content, but may be a result of some specific form or combination of calcium such as $CaCO_3$, or $CaSO_4$ being present or from the ratio of CaO to other constituents.

Effect of V_2O_5:U:CaO Ratio. A study of the chemistry of the possible reactions taking place during roasting indicated that the extraction of uranium was influenced by the amount of V_2O_5 in the ore and the amount of sodium vanadate in the calcine. When the ore contained no CaO a weight ratio of 5 parts V_2O_5 to 1 part U gave optimum extractions. Because, during roasting, free CaO combines with V_2O_5 to form calcium vanadate in preference to sodium vanadate, it is necessary to have

sufficient vanadium present to satisfy any uncombined CaO. The necessary weight ratio of V_2O_5 to CaO has been determined to be 3.2 to 1.

With these ratios it is possible to write a formula for the V_2O_5 content necessary to give high uranium extractions from natural ores. It is as follows:

$$V_2O_5\% = \text{or} > 3.2\ CaO\% + 5U\%$$

The significance of this may be stated as follows: When an ore contains the proper ratio of V_2O_5 to CaO and U or is raised to this ratio by additions or by blending, the effect of other variables such as roasting temperature, roasting time, and aging are minimized and uniformly high extractions of uranium can be obtained by the standard salt-roast carbonate-leach procedure.

Effect of Time of Roasting. The time of roasting was relatively unimportant, providing the optimum temperature was reached. After the roasting temperature was attained, roasting periods up to 30 minutes had little effect on the extraction of uranium. If the roasting temperature exceeded the optimum, overroasting and lowered extractions were noticeable, particularly in the finer particle sizes. Likewise, excessive roasting time (several hours) at the optimum temperature was not desirable.

Effect of Salt Additions. The addition of salt to a roast was not critical for the extraction of uranium. Though the optimum amount varied between 6 and 10 per cent for the different ores, the net effect of salt additions was fairly constant and contributed to some extent to the uranium extraction, although good results without salt were obtained on leaching the raw ore or on leaches of material roasted at low temperatures.

Salt additions were necessary for high extractions of vanadium. Normal salt additions gave vanadium extractions of 60 to 90 per cent under conditions deemed optimum for uranium.

Effect of Particle Size. The test data indicated that a decrease in particle size of the roaster feed from the standard 10 mesh to 48, 65, or 100 mesh resulted in increases in uranium extraction for all ores treated. The grinding and handling of minus 100-mesh ore was considered impractical in plant practice because of dust losses in both grinding and roasting. The finer material could be roasted at slightly lower temperatures and in shorter times but showed a tendency to pack as well as dust. The dense bed interfered with oxidation and proper roasting. Incipient fusion and caking were noticeable. It was considered that the economical balance and practicability of handling minus 10-mesh ore outweighed the small increase in extraction obtainable by leaching finely ground ore.

Effect of Air. Air was necessary during roasting if a satisfactory extraction of uranium was to be obtained. Sufficient oxidation during the roast and optimum results were obtained from all ores tested when an air-flow of 0.12 to 0.24 c.f.m. was maintained over the 100-gram charge. Excess aeration served only to increase dust losses and did not improve the uranium extractions.

Effect of Moisture in Air. Tests were made on Wild Steer Ore C-7 in which the only variable was the amount of moisture in the air used in roasting. Dry air proved better than moist air during roasting as regards final uranium extraction.

Leaching

The results of leaching an ore with sodium carbonate are dependent on the prior roasting treatment. The present discussion deals with ores that have been salt roasted at a temperature of 1560°F. The factors effecting leaching which have been evaluated are: time, temperature, pulp density, sodium carbonate concentration, and fineness of particle size. In addition, the applicability of other reagents such as ammonium carbonate and sodium bicarbonate was determined. The effect of elapsed time between roasting and leaching is discussed in a later section of this report on "A Study of the Aging of Calcines".

The standard leaching conditions employed were: 15 minutes agitation in hot 3 per cent sodium carbonate solution at a pulp density of 20 per cent of solids. The pulp was filtered immediately in a laboratory filter and washed four times with hot carbonate solution. The washings and filtrate were combined for analysis. The residue was dried, weighed, and assayed.

The test work was carried out by varying one condition at a time and results of tests were evaluated by means of the filtrate and residue assays.

Effect of Leaching Time. Tests investigating the effect of leaching time showed that the uranium extraction was rapid, being practically complete in 30 minutes. The extraction of uranium increased as the agitation leaching time increased from 1 minute up to 30 minutes.

In order to obtain data for longer periods of leaching, tests were made in which samples of roaster calcine were agitated in 3 per cent sodium carbonate at 195°F. for various periods of time up to 96 hours. The results are shown in Figure 1 in which the leaching time is plotted against the extraction. This figure shows that the percentage extraction remained practically constant in leaches of from 30 minutes to 24 hours duration after which the extraction drops off. Prolonged agitation was thought to foster the double decomposition of $Ca(OH)_2$ and Na_2CO_3 to $CaCO_3$ and NaOH with the subsequent partial precipitation of sodium diuranate from the solution. There was no apparent decomposition under the standard leach conditions.

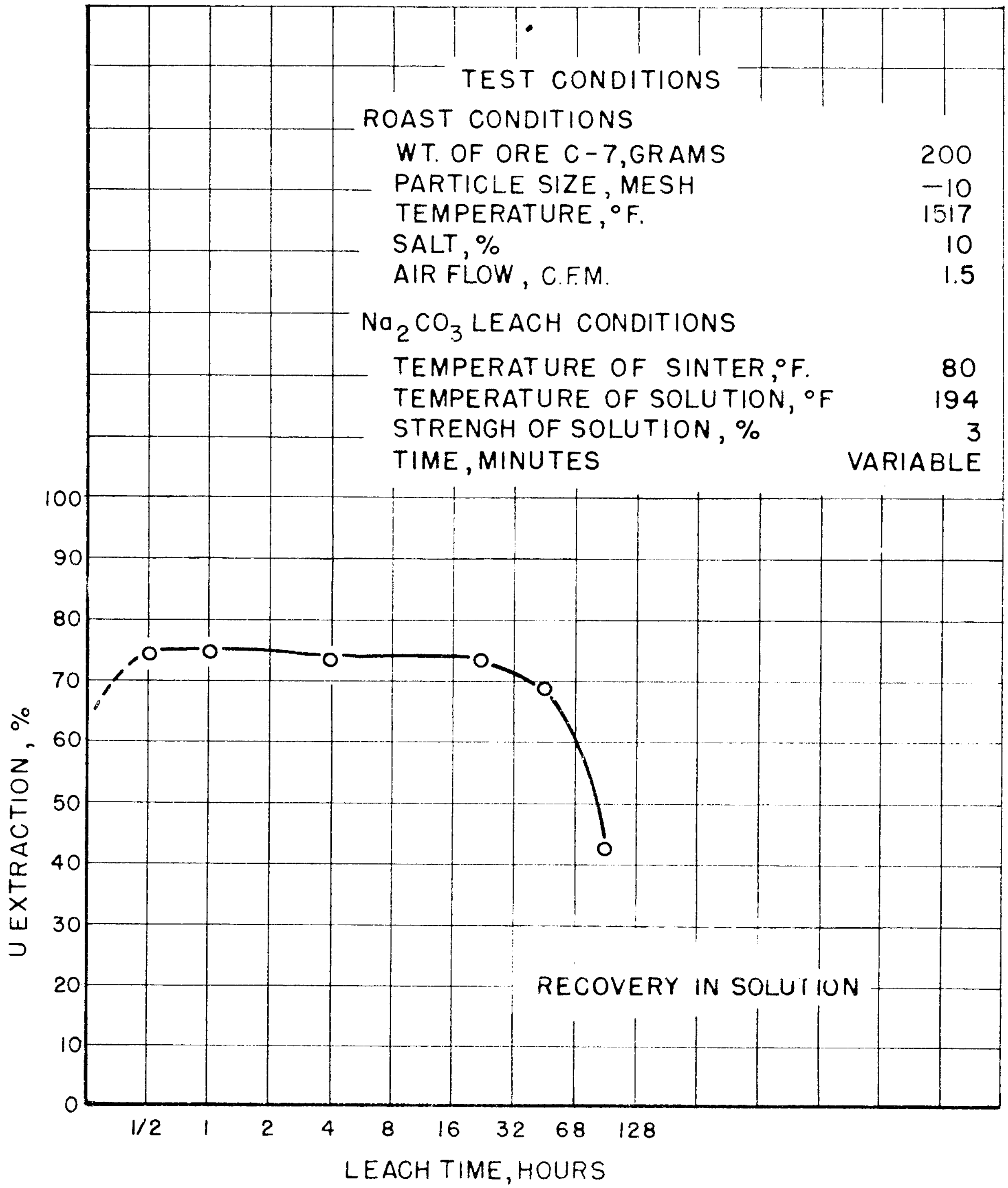

FIGURE 1. EFFECT OF LEACHING TIME ON EXTRACTION OF URANIUM

0-9341

Effect of Solution Temperature. The effect of leach solution temperature on the extraction of uranium from roaster calcine is shown in Figure 2. These data show the advantage of holding the leach solution as close to the boiling point as possible. An increase in temperature from 86 to 194°F. resulted in an increase of 5 per cent in the uranium extraction. The optimum temperature of the leach solution was determined to be 194°F. or above, although a lower temperature of 140°F. showed only a slight decrease in extraction. Theoretically, sodium uranate is more soluble in cold solution and the lower extraction may be a case of lower reaction rates rather than one of solubility.

The Effect of Pulp Density. The effect of pulp density in sodium carbonate leaching is shown in Figure 3. As the pulp density of the agitation leach decreased from 50 per cent of solids to 16 per cent of solids, the extraction of uranium increased as much as 12 per cent.

The decrease in uranium extraction with an increase in pulp density may result from the corresponding decrease in available sodium carbonate. The solubilization of the maximum amount of uranium requires a certain minimum amount and concentration of sodium carbonate. The use of dilute pulps as a method of improving the extraction would be comparatively simple to apply in a commercial plant and should be given some consideration.

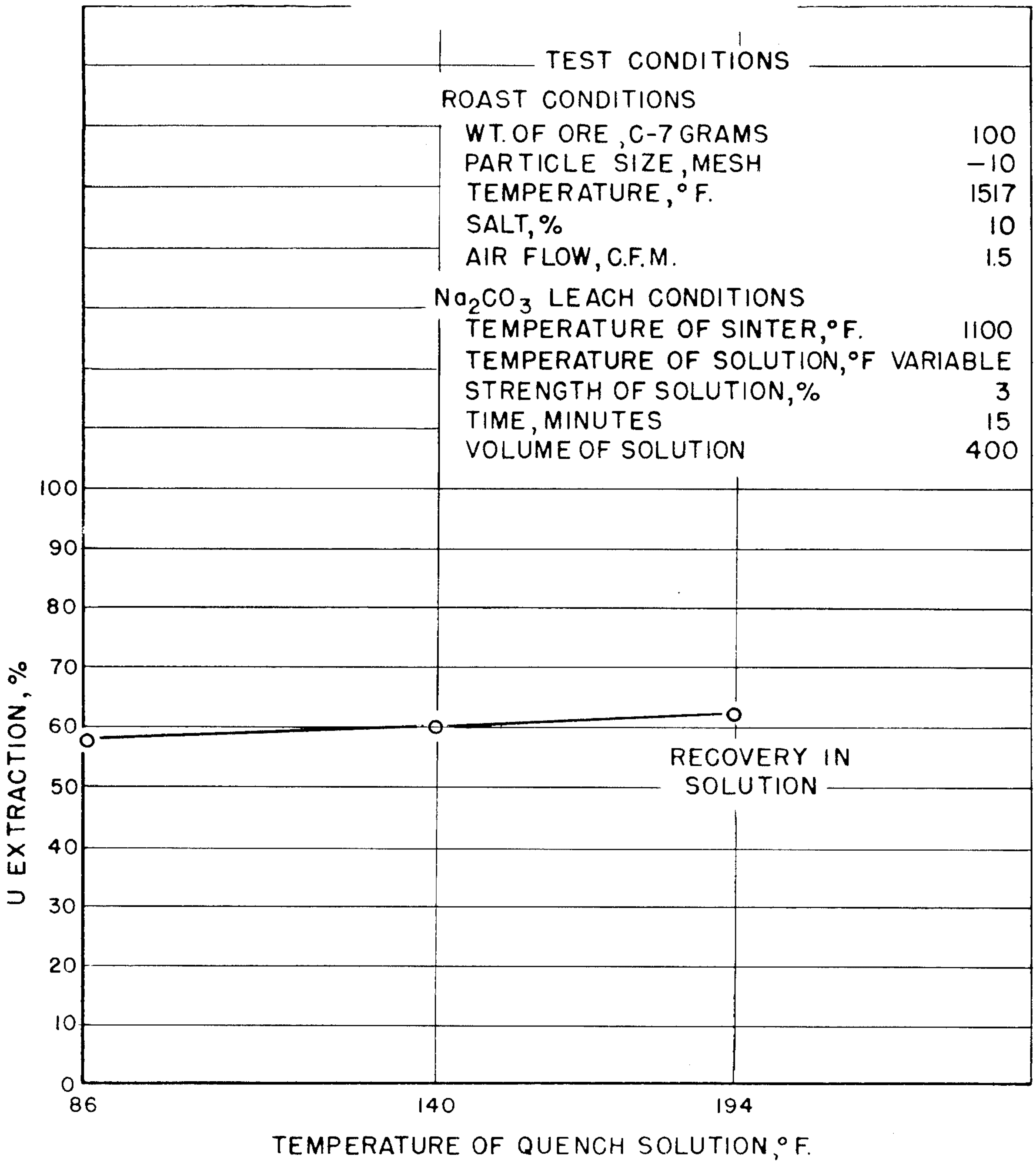

FIGURE 2. EFFECT OF TEMPERATURE OF LEACH SOLUTION ON RECOVERY OF URANIUM

0-9338

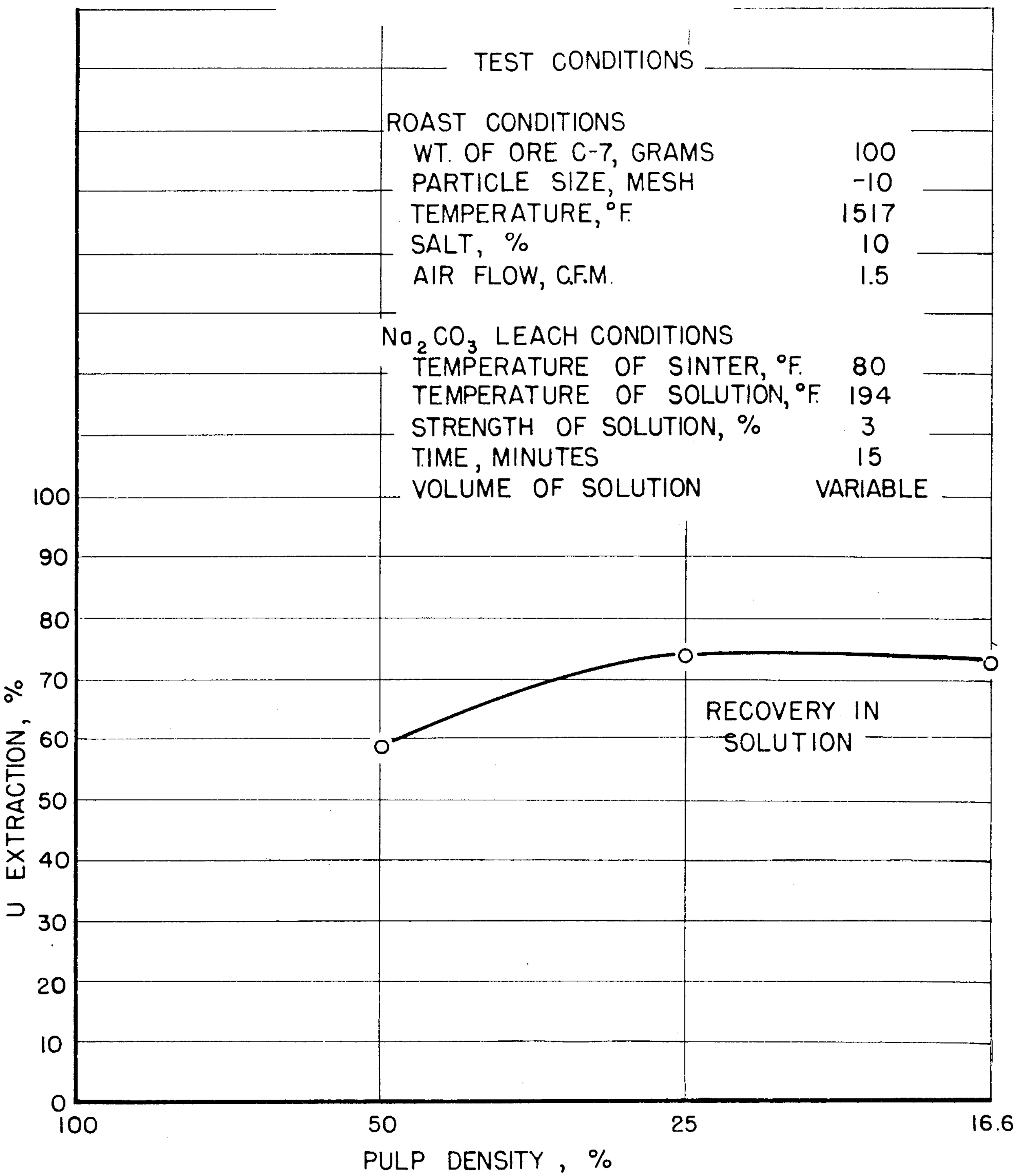

FIGURE 3. EFFECT OF PULP DENSITY ON EXTRACTION OF URANIUM

0-9336

Effect of Sodium Carbonate Concentration. A series of tests was made to determine the effect of Na_2CO_3 concentration in the leach solution on the extraction of uranium. The results of this work show that the uranium extraction increased as the concentration increased from 3 to 9 per cent. When the percentage of Na_2CO_3 was raised from 9 to 12, the extraction droppod off slightly. These data show the same result as lowering the pulp density and may be caused by the increased amount of sodium carbonate rather than its concentration. The slight drop in extraction at 12 per cent Na_2CO_3 concentration is not unexpected since the solubility of uranium carbonate in sodium carbonate solutions decreases as the sodium ion concentration increases.

Effect of Particle Size. Grinding the calcine, before leaching, from minus 10 mesh to minus 150 mesh, resulted in a small improvement in leaching efficiencies. However, grinding the quenched pulp in a ball mill for 30 minutes, which gave essentially a 100-mesh grind, gave a uranium extraction that was about the same as that obtained with the standard quench and leach.

In these tests the hot calcine from the furnace was divided into representative fractions, quenched in the standard manner in 3 per cent sodium carbonate solution and the hot pulp ground in a porcelain Abbe' pebble mill for 35 minutes at 33 per cent pulp density. The temperatures of the mill and pulp were held between 180 and 205°F. during

the grind and leach. Table 1 presents typical extractions obtained from these grinding-leaching tests.

TABLE 1. EXTRACTION OF URANIUM USING PEBBLE MILL GRINDING AND LEACHING OF ORE C-7 CALCINE

	Test 626	
	Standard Quench	35-Min. Grind
Minus 150 mesh in product, %	18.0	96.5
Extraction of uranium, %	73.6	74.8

<u>Sodium Carbonate Compared with Sodium Bicarbonate Leaching</u>. Two samples of salt-roasted calcine were leached, one with 3 per cent sodium carbonate solution, the other with 3 per cent sodium bicarbonate. The time, temperature, pulp density, and washing procedure were the same in each case. The resulting extractions indicated that there was no advantage in using sodium bicarbonate in place of sodium carbonate as a leaching agent. In the hot calcine from the furnace there was probably some HCl, $CaCl_2$, and other acid salts which would promote the formation of appreciable amounts of $NaHCO_3$ even in the leaching test in which Na_2CO_3 was the leaching agent.

On raw ore samples it may be of definite benefit to use the bicarbonate rather than the carbonate leach because neither HCl nor acid salts are present which promote the formation of $NaHCO_3$.

Sodium Carbonate Compared with Ammonium Carbonate Leaching. Leaching tests indicated that ammonium carbonate was as efficient as sodium carbonate in extracting uranium from carnotite ores. However, with ammonium carbonate leaches, the primary pregnant liquor can be boiled to remove the ammonium carbonate which lowers the pH of the solution to below 7 and results in the precipitation of 99.7 per cent of the uranium as a yellow precipitate which analyzes 45 per cent of uranium and 20 per cent of vanadium pentoxide. If the remaining vanadium could be recovered in a subsequent step, this method might become a relatively simple and inexpensive cyclic process, because the ammonium carbonate could be recovered for re-use.

Filtration

In any metallurgical process involving leaching, an important phase of the process is the separation of the pregnant liquor from the barren solids. In the case of salt-roasted carbonate-leached carnotite ores this problem is relatively simple because of the rapid settling and filtering rates of the pulps. However, if raw ores, such as the Bald Eagle Ore C-16, are to be leached directly, the problem of clarification becomes important. In this case the settling rates are very poor and filtration will probably be necessary.

While it is known that roasting the ores prior to leaching aids materially in increasing filtration rates, it is also true that the

roasting temperature must be limited if high uranium extractions are to be obtained. With these points in mind, an investigation was made of the interrelation of filtering rates, uranium extractions, and roasting temperatures for the Bald Eagle Ore C-16.

A study of the filtering characteristics of this ore followed the procedures outlined in Taggart's Handbook(1) using a filter-leaf frame of the standard design having 0.1 sq. ft. total area, covered with a canvas filter cloth which was connected to a vacuum receiver flask large enough to permit the use of a graduated cylinder to measure filtrate volumes.

The test procedure simulated the cycle of a drum filter with (1) a cake-forming stage during which the cloth was submerged in the pulp under vacuum; (2) a cake-drying stage during which the cloth and cake were out of contact with the pulp but still under the action of the vacuum; and (3) a cake-discharge stage.

The ore was ground to pass 42 mesh because coarser particles did not remain in suspension. Tests were run on the unroasted material and on samples that had been roasted at 390°F., 750°F., and 1110°F., respectively. Two thousand grams of ore was mixed with 1000 ml. of 3 per cent sodium carbonate, resulting in a pulp density of 66 per cent.

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(1) Handbook of Mineral Dressing, A. F. Taggart, John Wiley & Sons, Inc., 1947, page 19-167.

The tests were carried out using hot pulp at a pH of 10 to 10.3 and a vacuum of 20 inches of mercury. The pulp density was checked by sampling after each test run.

Table 2 presents the results on the filterability of samples of Ore C-16 which shows that the filtering time for a definite weight of filter cake decreased from 8 minutes to 6 seconds as the roasting temperature of the ore was increased from room temperature to 1110°F. The data also show that as the roasting temperature was increased the speed and efficiency of the drainage of the filter cakes increased and the final moisture contents decreased from 20 to 16 per cent. The filter cake from the material which had been roasted at 1110°F. prior to leaching drained 2-1/2 times as fast as an equal weight of cake from the ore which had been leached without prior roasting.

The increase in filtering rate obtained by roasting the ore prior to leaching is shown graphically in Figure 4. The pulp of the roasted material formed a filter cake more rapidly than the unroasted ore pulp and this factor increased as the roasting temperature increased. The filterability of pulps of ore roasted at temperatures above 1110°F. would undoubtedly remain excellent. Therefore, it would be advantageous to use the highest roasting temperature commensurate with satisfactory uranium extraction.

As shown in Figure 5 (The Effect of Roasting Temperature on Extraction of Uranium) the maximum uranium extraction on this ore was

TABLE 2. FILTRATION TEST DATA ON BALD EAGLE No. 1 ORE C-16

1	2	3	4	5	6	7	8
						Variable Filtration Cycle (2)	
Sample No.	Roasting Temp., °F.	Average Time To Reach a Constant Wt. of Cake, Minutes	Average Time To Drain Filter Cake, Minutes	Average Moisture in Cake, %	Approx. Weight of Cake Filtered,(1) Lbs. per sq. ft. per 24 hrs.	Time of Cycle, Minutes	Approx. Weight of Cake Filtered and Dried, Lbs. per sq. ft. per 24 hrs.
1	Raw Ore	8	20	20	1000	28	200
2	390	3	14	18	1600	17	330
3	750	1	14	17	2700	15	370
4	1110	0.1	8	16	5500	8.1	690

(1) Based on a uniform cycle of 2 minutes' duration, one minute for filtration and one minute for drainage for all four samples. The filter cakes would not be completely dry in this drainage time of one minute. This is merely a comparison of filter capacities assuming equal filtration and drainage times for the different ores.

(2) This estimation of filter capacities is based on the complete filtration and drainage time (in Column 7) necessary for a cycle to produce a given weight of cake from each sample.

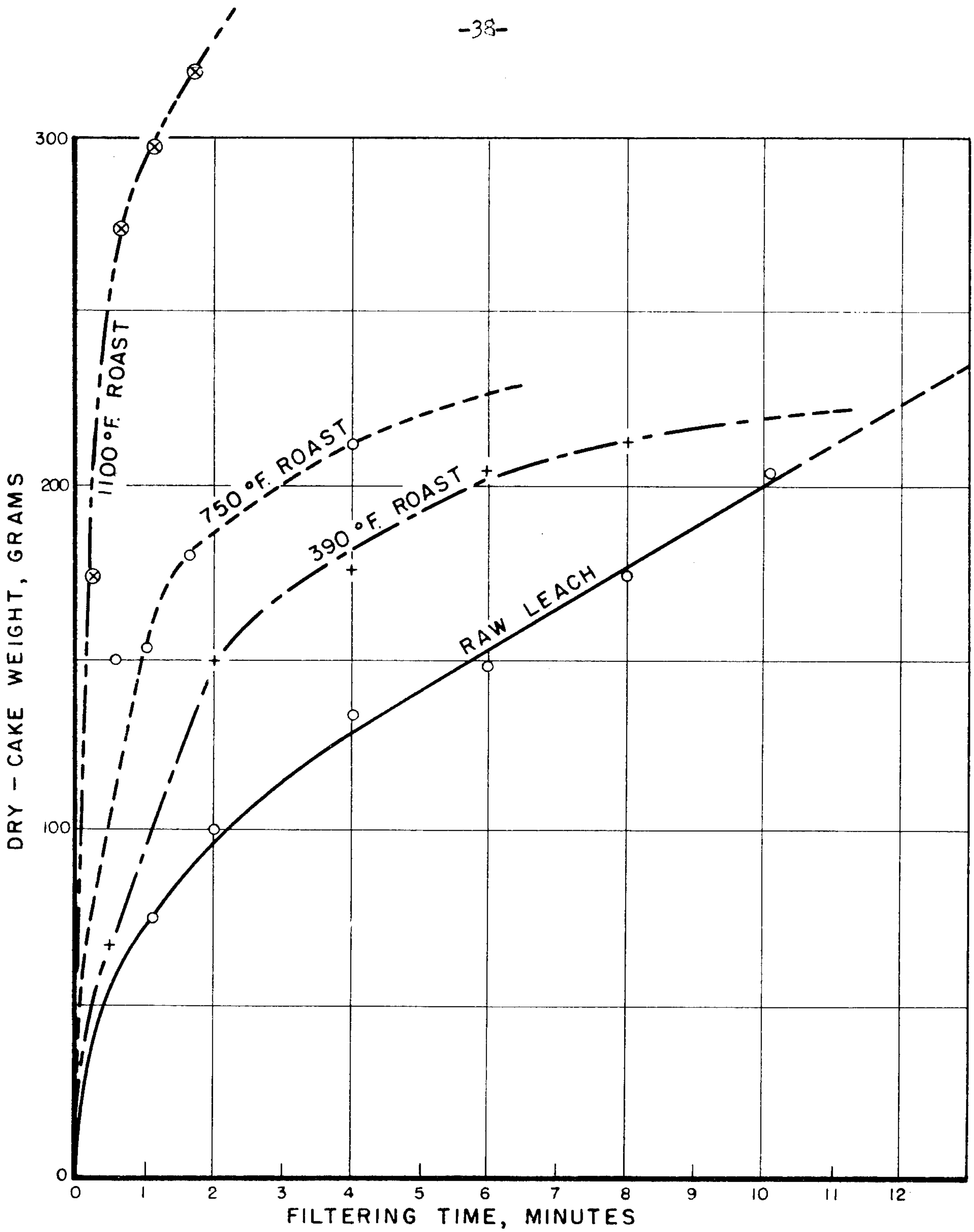

FIGURE 4. RESULTS OF FILTERING TESTS ON BALD EAGLE ORE C-16, FILTERING TIME VS. WEIGHT OF CAKE

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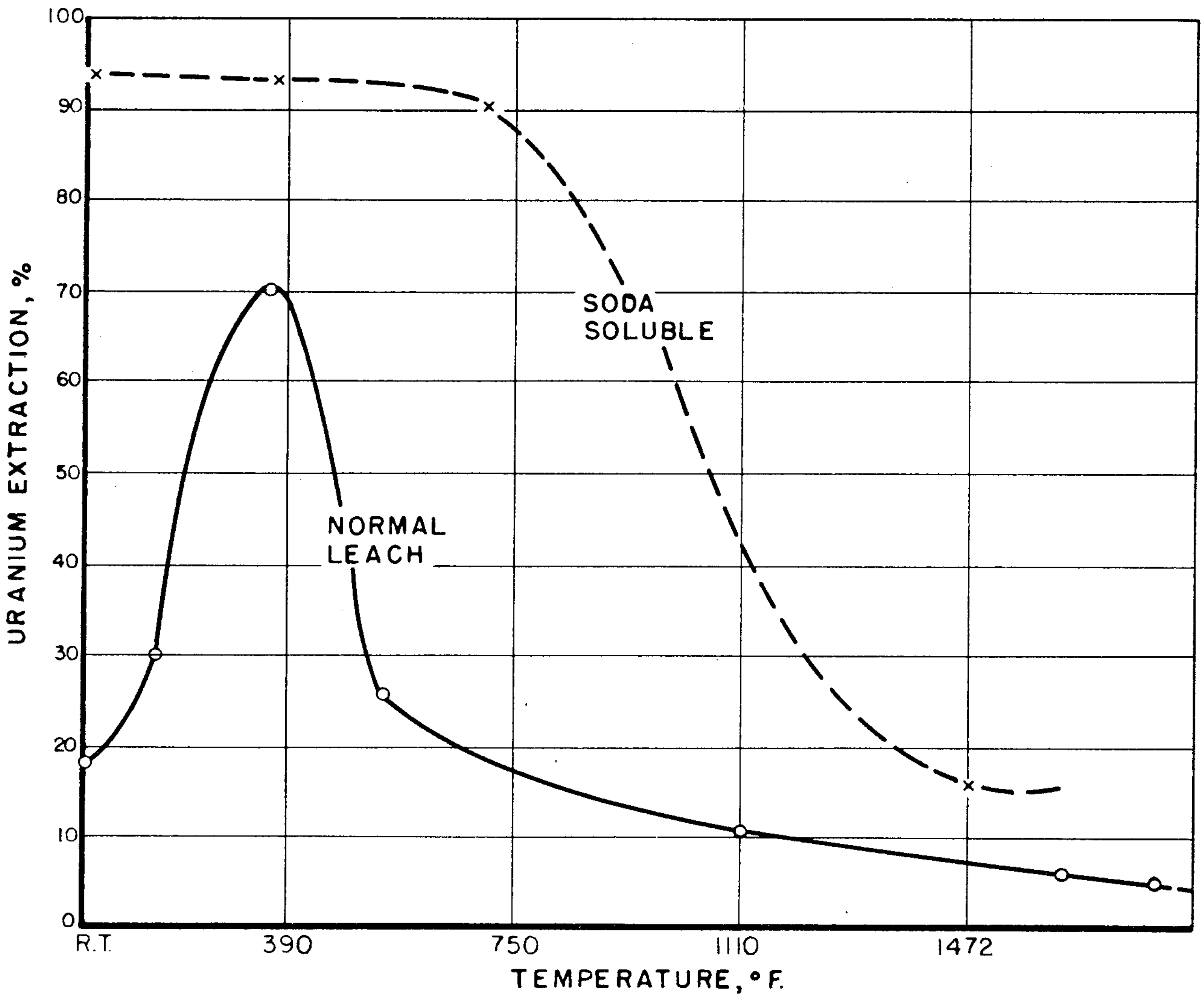

FIGURE 5. EFFECT OF ROASTING TEMPERATURE ON EXTRACTION OF URANIUM FROM ORE C-16.

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obtained from ore roasted at 390°F. At 750°F. the rate of dissolution dropped, but the ultimate extraction of the uranium was still above 90 per cent. Longer leaching times should give equally good extractions plus more rapid filtering on ore roasted at 750°F.; but, if fairly rapid leaching is desired, the lower roasting temperature should be employed. If sufficient plant filter capacity were available, it would be advisable to roast at 390°F. in order to secure faster dissolution even though the filtering rates were slower than from a roast at 750°F. The filtering rate of material roasted at 390°F. was still about 50 per cent faster than that obtained with a raw ore leach.

The Effect of Associated Elements on the Extraction of Uranium

Introduction

This section of the report covers the experimental work on the effect of associated elements[1] on the extraction of uranium from carnotite ores. This work was confined to the standard salt-roast carbonate-leach process as practiced at the Monticello plant.

Prior to the investigation of the effect of extraneous elements, work was conducted to determine the effect of the separate variables of the salt-roast carbonate-leach process on several ores as already described. These variables included roasting time, roasting temperature,

(1) For this report, associated elements include any substance occurring in the natural ores which may or may not be detrimental to the extraction of uranium.

air flow, particle size of the ore, effect of salt, effect of pyrite, aging of the calcines, leaching time, temperature and strength of the leach solution, and pulp density of the leach solution. The optimum conditions for the treatment of each ore were established after the study of each variable singly. After comparing these results for 15 individual ores, two facts were evident as follows:

(1) The optimum soda-soluble extraction of uranium was different for each ore.

(2) Different optimum roasting and leaching conditions were required for each ore.

These deductions indicated that, in addition to the other variables, the extraneous elements occurring in the ores influenced their response to treatment by this process. Therefore, a study of the effects of these extraneous elements became imperative and work was begun to determine their individual effects in synthetic ore samples(1). The uranium compounds that were used in making up the synthetic ores were: the oxide, U_3O_8; the double salt, $Na_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$; the diuranate, $Na_2O \cdot 2UO_3 \cdot 2H_2O$; the tricarbonate, $Na_4UO_2(CO_3)_3$, and handpicked specimens of carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$.

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(1) The synthetic ore samples consisted of 100 grams of Ottawa silica sand, as a base, to which various soda-soluble uranium compounds were added in amounts equal to 0.32 gram of uranium.

Preliminary Test Work on Synthetic Ores

Preliminary test work was instigated to determine the effect of salt roasting on the solubility of uranium in synthetic ores. Prior to roasting, the uranium in the compounds investigated could be extracted completely by leaching in hot sodium carbonate or sodium bicarbonate solutions. However, after roasting at 1560°F., only 15 to 30 per cent of the uranium in any of the synthetic ores was soluble. These tests led to two major conclusions as follows: (1) that salt roasting was detrimental to the extraction of uranium from these compounds, and (2) that some of the accompaning elements in the natural ores must be beneficial to the extraction of uranium in the salt-roasting process, since higher extraction values were obtained from the natural ores than from the synthetic ores.

Starting Point for the Determination of the Effect of Associated Elements

Since much of the preliminary work was done on a synthetic ore containing sodium uranyl tricarbonate, further work was continued using it as the uranium-bearing compound. A normal salt-roast[1] carbonate-leach treatment was first given to this ore before any compounds were added. This treatment resulted in a base-line extraction of 19 per cent of the uranium.

Using this base line for comparison, the effects of adding associated elements to the synthetic ore were evaluated. The data in

(1) Roasted at 1560°F. for 30 minutes.

Table 3 show the salt-roast carbonate-leach results when single associated compounds were added to a synthetic ore which contained 0.32 per cent of uranium as sodium uranyl tricarbonate and 10 per cent of salt. The compounds chosen are those found most frequently in the natural ores and the amounts added were to agree with the amounts occurring in natural ores. For purposes of clarity, the effects of these compounds are cataloged in three groups: (1) detrimental, (2) intermediate, and (3) beneficial, as follows:

Detrimental	Intermediate	Beneficial
MgO	CaO	Na_3PO_4
Al_2O_3		SO_2
Fe_2O_3		P_2O_5
CaF_2		V_2O_5

Additions of from 0.5 to 5.0 per cent of the detrimental compounds resulted in values lower than the original base line uranium extraction of 19 per cent. The intermediate compound, when added in quantities of 5 per cent increased the extraction slightly. The addition of from 0.5 to 5.0 per cent of the beneficial impurities raised the extraction to 50 per cent or more. It is believed that soluble uranium compounds are formed with the beneficial impurities. Examples of such compounds are soluble uranyl sulphate or sodium uranyl sulphate, uranyl vanadate or sodium uranyl vanadate, and sodium uranyl phosphate.

TABLE 3. EFFECT OF SINGLE COMPOUNDS ON SODA-SOLUBLE URANIUM FROM SALT-ROASTED SYNTHETIC ORE[1]

Compound Added	Compound Weight, Per Cent	Uranium Extraction, Per Cent
None	-	19
MgO	0.5	3
"	1.5	5
"	5.0	18
Al_2O_3	0.5	4
"	1.5	5
"	5.0	9
Fe_2O_3	0.5	17
"	1.5	15
CaF_2	0.5	nil
"	1.5	nil
"	5.0	nil
CaO	0.5	4
"	1.5	5
"	5.0	32
Na_3PO_4	0.5	21
"	1.5	46
"	5.0	54
FeS_2 (pyrite)	0.5	20
"	1.5	54
"	5.0	85
SO_2	0.12 c.f.m.	92
P_2O_5	0.5	65
"	1.5	74
"	5.0	100
V_2O_5	0.5	47
"	1.5	100
"	5.0	100

(1) Synthetic ore made up from 100 grams silica sand and 0.32 gram uranium as sodium uranyl tricarbonate.

Further investigation of the soluble sulphates has not been made because these reactions do not occur in the normal salt-roasting process. However, further work has been carried out to investigate the reactions with V_2O_5 and P_2O_5.

Studies of the Reaction with V_2O_5

Figure 6 shows the effect of V_2O_5 additions on uranium extractions from a synthetic ore. Prior to roasting at 1560°F., V_2O_5 additions of from 0.1 to 5.0 per cent were made to a standard synthetic ore composed of 0.32 per cent of uranium as sodium uranyl tricarbonate, 100 grams of silica sand and 10.0 grams of salt. The results show that for additions of V_2O_5 of between 0.2 and 1.5 per cent, the uranium extractions were almost directly proportional to the amount added, and a straight-line function is represented. With 1.5 and 5.0 per cent of V_2O_5 additions, complete solubilization of uranium took place. The addition of 1.5 per cent of V_2O_5, the minimum amount for complete solubility of uranium, represented a V_2O_5 to uranium ratio of about 5 to 1. Additional tests were made to determine the validity of this ratio by adding proportional amounts of V_2O_5 to synthetic ores containing 0.16 and 0.64 per cent of uranium. For complete solubilization of uranium in these tests, a 5 to 1 ratio of V_2O_5 to uranium was required for the synthetic ore containing 0.16 per cent of uranium and a 6 to 1 ratio was required for the synthetic ore containing 0.64 per cent of uranium. Such a ratio gave substantially complete vanadium extractions.

STANDARD CONDITIONS

100.0 GRAMS SILICA SAND
0.32 PER CENT URANIUM
10.0 GRAMS NaCl

ROASTING:

TEMPERATURE, °F. — 1560
TIME, MIN. — 30
AIR, C.F.M. — 0.12

LEACHING:

TEMPERATURE, °F. — 200
REAGENT Na_2CO_3, % — 6
AMOUNT, ML. — 800
TIME, MIN. — 30

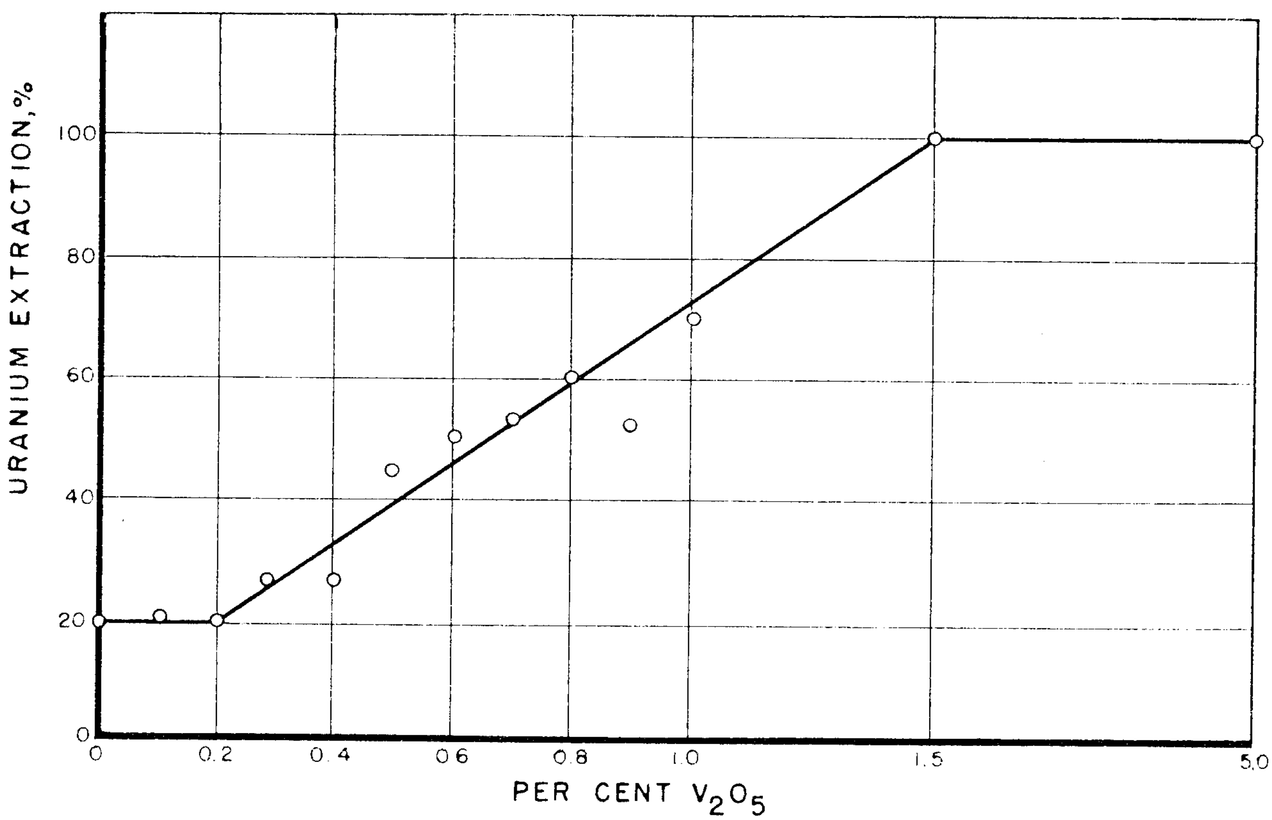

FIGURE 6. THE EFFECT OF V_2O_5 ADDITIONS ON URANIUM EXTRACTIONS FROM A SYNTHETIC ORE.

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Effect of Associated Elements on a Synthetic Uranium-Vanadium Ore

Having established the importance of V_2O_5 as a beneficial element, the effect of associated elements on the extraction of uranium from a synthetic uranium-vanadium ore[1] was studied. This work was similar to the study of associated elements in synthetic ores containing only uranium.

Table 4 shows the effect of single compounds on the soda-soluble assays for the extraction of uranium from a salt-roasted synthetic uranium-vanadium ore. Before the addition of any impurities, the base-line extraction of uranium was 100 per cent as compared to 19 per cent for the synthetic ore containing only uranium. Also, before roasting, the extraction of vanadium in the uranium-vanadium synthetic ore was 100 per cent. These results show that, with the exception of lime (CaO), the compounds, MgO, Al_2O_3, Fe_2O_3, CaF_2, $CaSO_4$, and $Ca_3(PO_4)_2$, were only moderately detrimental to either the uranium or the vanadium extraction, indicating decreases ranging from 10 to 30 per cent.

In the case of CaO, experimental work showed a marked drop in the uranium extraction when increasing amounts of it were added. This drop did not take place with the other salts of calcium, CaF_2, $CaSO_4$, and $Ca_3(PO_4)_2$. This suggested a highly reactive nature for the oxide of calcium, whereas the other salts of calcium are less reactive and had less effect. Attempts were made to fix the CaO by adding compounds

(1) The synthetic uranium-vanadium ore consisted of 100 grams of Ottawa silica sand, as a base, to which 0.32 gram of uranium as sodium uranyl tricarbonate and 2 grams of vanadium pentoxide were added.

TABLE 4. EFFECT OF ADDED COMPOUNDS ON SODA-SOLUBLE URANIUM FROM SALT-ROASTED SYNTHETIC URANIUM-VANADIUM ORE[1]

Added Compound	Compound, Weight Per Cent	Extraction, Per Cent	
		Uranium	Vanadium
None	-	100	100
MgO	0.5	77	82
"	1.5	87	87
CaO	0.5	63	89
"	1.5	44	80
"	5.0	33	54
"	15.0	25	66
Al_2O_3	0.5	-	82
"	1.5	85	85
"	5.0	87	79
"	15.0	79	78
Fe_2O_3	0.5	80	88
"	1.5	78	81
"	5.0	77	88
CaF_2	1.5	88	88
"	5.0	79	80
$CaSO_4$	0.5	71	86
"	1.5	74	79
$Ca_3(PO_4)_2$	0.5	72	90
"	1.5	70	88
"	5.0	74	88

(1) Synthetic ore made up of 100 grams silica sand, 0.32 gram of uranium as sodium uranyl tricarbonate, and 2 grams of V_2O_5.

to the synthetic uranium-vanadium ore which would form more stable calcium compounds and prevent the highly detrimental effect of the free CaO.

Studies on the Fixation of CaO

Table 5 shows the results of tests on CaO fixation in a synthetic ore. The compounds Na_3PO_4, Na_2SO_4, and Na_2SO_3 indicate little if any tendency toward fixation; the uranium extractions were roughly equal to those obtained without their addition. In the case of P_2O_5 and V_2O_5, increasing amounts of these compounds were beneficial indicating the formation of a stable calcium salt not detrimental to the uranium extraction.

A comparison can be made of the advantages and disadvantages of using P_2O_5 instead of V_2O_5 to effect CaO fixation. The results from Table 5 show that in a uranium-vanadium synthetic ore containing 5 per cent of CaO, a smaller amount of P_2O_5 than of V_2O_5 was required to obtain a given uranium extraction. However, part of the P_2O_5 was soluble in the sodium carbonate leach solution. Tests showed that P_2O_5 appeared to be detrimental to the precipitation of uranium from the pregnant solution, being partially co-precipitated with the uranium during that step. Therefore, trouble would be involved in obtaining a complete separation of uranium and phosphorus from the leach solution. A second disadvantage in

TABLE 5. EFFECT OF CaO FIXATION ON SODA-SOLUBLE URANIUM FROM SALT-ROASTED SYNTHETIC URANIUM-VANADIUM-CALCIUM ORE(1)

Added Compound	Compound, Weight Per Cent	Extraction, Per Cent Uranium	Extraction, Per Cent Vanadium
None	-	33	60
P_2O_5	0.5	32	49
"	1.5	30	54
"	4.4	75	-
"	5.0	75	77
"	5.5	86	100
"	10.0	84	94
Na_3PO_4	0.5	33	62
"	1.5	35	56
"	5.0	51	66
Na_2SO_4	0.5	nil	80
"	1.5	15	62
"	5.0	15	72
Na_2SO_3	0.5	30	70
"	1.5	31	65
"	5.0	21	55
V_2O_5	5.0	45	60
"	10.0	79	74
"	15.0	83	89
"	20.0	81	89
"	25.0	90	91

(1) Synthetic ore composed of 100 grams of silica sand, 0.32 gram of uranium as sodium uranyl tricarbonate, 2 grams of V_2O_5 (unless otherwise specified), and 5 grams of CaO.

the use of P_2O_5 is that it is extremely hygroscopic. This property would cause difficulty in handling and would prevent the uniform distribution of the P_2O_5 in the ore sample.

X-Ray Diffraction Studies

To determine the physical and chemical changes that samples containing uranium and vanadium undergo during the salt-roasting operation, X-ray diffraction studies were made on head samples, roasted products, and leached residues of various uranium-bearing compounds. These compounds were examined singly, or in combination with various proportions of silica, salt, and vanadium pentoxide.

Because only a short period of time was available for this study, the work was of a cursory nature and sufficient data were not gathered to present a complete picture of the changes that occur during roasting and leaching. Two significant facts were evident: (1) the phase changes of different compounds were not identical[1] and (2) there was a complete absence of sodium diuranate in the roasted product after the roasting operation[2].

Further X-ray diffraction work is necessary to give a more complete report on the phase changes of the uranium and the identification of each X-ray pattern.

(1) The uranium patterns of various uranium-bearing compounds after roasting and/or leaching were compared by X-ray diffraction methods. However, no indication was given that these patterns were identical.

(2) The X-ray diffraction data for synthetic ores showed that the uranium was not converted to sodium diuranate as is frequently suggested in the literature.

Effect of Associated Elements on the Extraction of Uranium and Vanadium from Natural Ores

Having established the significance of V_2O_5 as a beneficial compound in synthetic ores, attention was given to the determination of the effects of V_2O_5 on the extraction of uranium and vanadium from natural ores. Sufficient V_2O_5 was added to the natural ores to combine with all of the calcium present to form calcium metavanadate plus enough additional V_2O_5 to furnish a 5:1 ratio of V_2O_5 to uranium for each ore. The results of this work as well as the extractions of uranium and vanadium prior to the V_2O_5 addition are given in Table 6. A comparison of these results showed a marked improvement in the extractions of the uranium when V_2O_5 was added, particularly for the Bald Eagle C-16 and Blend C ores. The uranium extractions by agitation-leaching were raised from 15 to 73 per cent for the Bald Eagle ore, and from 45 to 84 per cent for the Blend C ore, with soda-soluble amounts of 76 and 92 per cent, respectively.

The results of experimental work on the effect of roasting temperature and roasting time on the extraction of uranium from natural ores containing additional V_2O_5 are given in Table 7. The first set of figures shows the extractions of uranium and vanadium when the roasting time was held constant and the roasting temperature was varied between 1200 and 1650°F. These results show a general rise in the extraction of uranium and vanadium for Ores C-8, C-16, and Blend C as the temperature

TABLE 6. EXTRACTION OF URANIUM AND VANADIUM FROM NATURAL ORES WITH AND WITHOUT V_2O_5 ADDITION

Ore	V_2O_5 Addition, Per Cent of Ore Wt.	Uranium Extraction(1), Per Cent	Soda-Soluble Uranium(2), Per Cent	Vanadium Extraction(1), Per Cent
Wild Steer C-7	0	80	-	-
"	0.66	92	96	93
Gyp Valley C-8	0	50	-	-
"	8.0	83	92	88
Bald Eagle C-16	0	15	-	-
"	57.0	73	76	62
Radium 7 C-20	0	70	-	-
"	7.0	83	92	87
Blend C(3)	0	45	-	-
"	9.0	84	92	85

(1) Extraction based on 30-minute agitation leach of minus 10-mesh ore at 20 per cent solids in 194°F., 3 per cent sodium carbonate solution.

(2) Extractions based on 60-minute agitation leach of minus 100-mesh ore at 3 per cent solids in 194°F. 6 per cent sodium carbonate solution.

(3) Blend C composed of:

15.92 per cent Wild Steer Ore C-7
9.56 per cent Garbutt Group Ore C-9
15.92 per cent Gyp Valley Ore C-8
8.51 per cent Yellowbird Ore C-13
8.51 per cent Henry Mt. Ore C-14
31.90 per cent Ownbey Ore C-15
9.68 per cent Bald Eagle Ore C-16

TOTAL 100.00

Blend C contained:

0.30 per cent uranium
2.23 per cent of vanadium
3.00 per cent of CaO

TABLE 7. THE EFFECT OF ROASTING TEMPERATURE AND ROASTING TIME ON THE SODA-SOLUBLE EXTRACTION OF URANIUM AND VANADIUM FROM NATURAL ORES CONTAINING ADDITIONAL V_2O_5(1)

Roasting Temp., °F.	Roasting Time, Min.	Uranium Extraction(2), Per Cent			Vanadium Extraction(2), Per Cent		
		Ore C-8	Ore C-16	Blend C	Ore C-8	Ore C-16	Blend C
1200	30	65	58	69	49	66	64
1290	30	66	52	63	51	63	70
1470	30	81	64	74	64	56	64
1560	30	93	76	87	86	64	85
1650	30	63	67	87	48	39	86
1560	1	78	67	76	69	40	70
1560	5	-	69	73	-	58	68
1560	15	84	75	85	75	38	78
1560	30	93	76	87	86	64	85
1560	60	85	61	80	76	47	79

(1) V_2O_5 additions were added to 100-gram samples of Ores C-8, C-16, and Blend C in amounts of 8.0, 57.0, and 9.0 grams, respectively.

(2) Extractions based on 60-minute leach of minus 10-mesh ore at 20 per cent solids in 194°F., 6 per cent sodium carbonate solution.

was increased from 1200 to 1560°F. At 1560°F., maximum values for both the uranium and vanadium extraction were obtained for all three ores. A higher temperature of 1650°F. resulted in a drop in the uranium and vanadium extraction for Ores C-8 and C-16, and no change for Blend C. Figure 7 shows, graphically, the effect of roasting temperature upon the extraction of uranium for Ores C-8, C-16, and Blend C after the addition of V_2O_5.

The second set of figures shows the results on the extraction of uranium and vanadium when the roasting temperature was held constant at 1560°F. and the roasting time was varied between 1 and 60 minutes. These results show a rise in the extraction of uranium and vanadium for Ores C-8, C-16, and Blend C as the roasting time was increased to 30 minutes. For a 30-minute roasting time, maximum values for both the uranium and vanadium extraction were obtained for all three ores. A longer roasting time of 60 minutes proved detrimental and the uranium and vanadium extractions for all three ores dropped. Ores C-8, C-16, and Blend C were chosen for a roasting temperature study because of the wide variation of their optimum roasting temperatures prior to the addition of V_2O_5. The optimum roasting temperatures for these ores without the addition of V_2O_5 were: (1) Ore C-8, between 1380 and 1470°F., (2) Ore C-16, 390°F., and (3) Ore Blend C, 1560°F. This wide temperature variation is undesirable in plant practice because of the necessity for

STANDARD CONDITIONS

ROASTING:		LEACHING:	
TEMPERATURE	— VARIABLE	TEMPERATURE, °F	— 200
TIME, MIN.	— 30	REAGENT Na_2CO_3, %	— 6
AIR, C.F.M.	— 0.12	AMOUNT, ML.	— 800
		TIME, MIN.	— 30

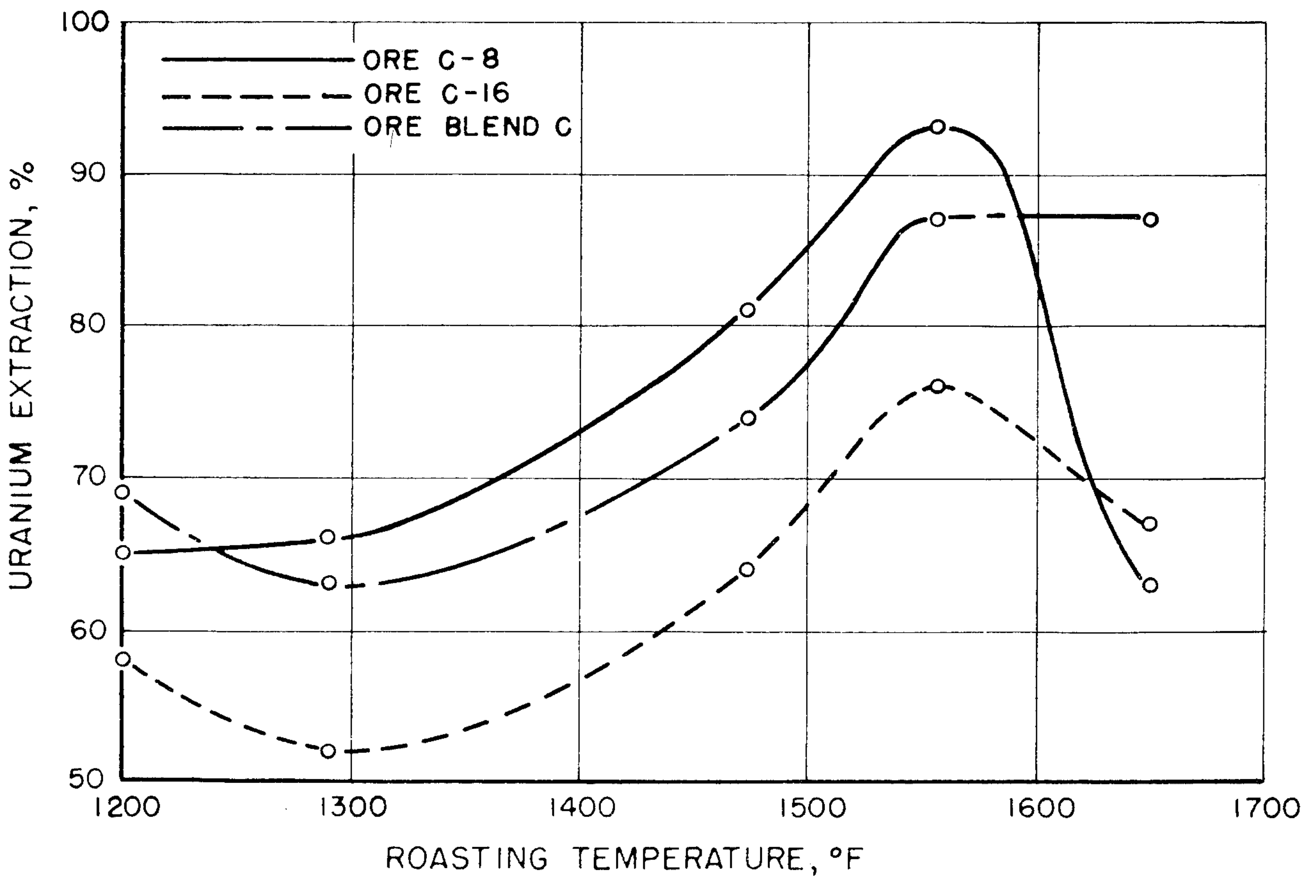

FIGURE 7. THE EFFECT OF STABILIZING THE OPTIMUM ROASTING TEMPERATURE FOR NATURAL ORES CONTAINING V_2O_5

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a separate roasting treatment for each individual ore. The danger of overroasting or underroasting would prevent the blending of such ores. This would cause continuous plant readjustments as the plant feed changed, resulting in extra delay and expense.

However, identical optimum roasting temperatures and roasting times for each ore were obtained when the correct V_2O_5:U:CaO ratio was maintained. These results from Table 7 may be summarized as follows:

Ore[1]	Optimum Roasting, Temp., °F.	Optimum Roasting Time, Min.	Uranium Extraction, Per Cent
C-8	1560	30	93
C-16	1560	30	76
Blend C	1560	30	87

Figure 7 illustrates these data by showing the optimum extraction peaks for Ores C-8, C-16, and Blend C, all of which containing a proper V_2O_5: U:CaO ratio.

The importance of obtaining identical optimum roasting temperatures and roasting times can readily be understood. With a suitable V_2O_5:U:CaO ratio, there is a very good possibility of blending the ores for furnace feed. With identical roasting temperatures, the dangers of underroasting or overroasting any one ore in the blend would be at a minimum, and an over-all increase in the extraction of uranium in the blend could be expected. Also, the plant operation would be simplified, and roasting could be carried out under the same conditions at all times.

(1) V_2O_5:U:CaO ratio of all ores adjusted by adding V_2O_5.

A Study of the Aging of Calcines

Introduction

Early in the experimental work on the recovery of uranium from carnotite ores by the salt-roast carbonate-leach process, it was observed that the manner in which calcines were handled between the roasting and leaching operations had a marked effect on the percentage of uranium extracted. The extractions obtained from presumably similar tests were not always comparable and it was difficult to correlate the results from large and small scale tests. Calcines that were allowed to stand for several hours before leaching gave lower uranium extractions than those that were leached as soon as possible after they were removed from the furnace. This loss in uranium extraction was attributed to aging.

Aging, as used in this report, is defined as the change that occurs in a calcine after roasting, which adversely affects the subsequent extraction of uranium by carbonate leaching. The nature of aging was investigated with the objective of developing ways of overcoming it. This section of the report presents the results of numerous tests with Wild Steer ore which were made to evaluate the variables that influence aging.

Equipment and Procedure

The muffle type furnace used in calcining the ore for the aging tests was designed to permit the maximum control of all variables and to give reproducible results. It was electrically heated and consisted of a rectangular nickel shell wound with resistance wire and then encased in K-20 insulating brick. The furnace was divided into three sections suitable for roasting three samples simultaneously. Each section was provided with separate air inlets, gas outlets, and rabbles. The rabbles were so constructed that they could be operated together or separately and either mechanically or by hand. Sample pans and rabble arms were made of black iron. Individual thermocouples were placed in each charge and temperatures were recorded with a Micromax recorder.

The procedures used in roasting, quenching, and leaching in the standard, or control, tests were similar to procedures used in other work on carnotite ores and closely approximated those used at the plant at Monticello, Utah. A batch of dry ore was crushed to minus 10 mesh, mixed with 10 per cent by weight of salt, and samples of about 500 grams were cut from this mixture for each roasting test. The furnace was heated to 1100°F. prior to charging the samples of ore. The rate of heating was regulated from the time the samples reached 930°F. until the final roasting temperature was reached. The roasting temperature was about 1560°F.(1) and the roasting time, which was measured from the time

(1) The optimum temperature in this furnace for the extraction of uranium from Wild Steer Ore.

the sample reached the roasting temperature until the calcine was discharged, was 15 minutes. The ore was rabbled in an oxidizing atmosphere of air during roasting. The amount of air entering the furnace was regulated by a rotameter and was then either dried before entering the furnace or passed through a hygrometer to measure the relative humidity.

After the ore was discharged from the furnace, it was necessary to let it cool for at least five minutes before it could be quenched in the carbonate solution because of the violent action which would otherwise take place. This five-minute cooling period was part of all "immediate" or standard quench procedures.

The aging period was measured from the time the hot calcine left the furnace until the beginning of the quenching or leaching procedure. The calcine was quenched and/or leached in a 3 per cent solution of sodium carbonate at a pulp density of 25 per cent. After a 30-minute period of agitation leaching at a temperature of 190°F. the pulp was filtered and the residue was washed with four 200-ml. washes of 3 per cent sodium carbonate solutions. The amount of uranium extracted was determined by assaying both the filtrates and residues.

In those tests in which three samples were roasted simultaneously, one sample was used as a control and was subjected to the standard quench and leaching procedure in a 3 per cent sodium carbonate leach solution. The other two samples were used to evaluate the variables thought to influence aging.

The Effect of Rate of Cooling

Previous work had shown that when samples of the Wild Steer ore were subjected to the standard procedure of roasting and quenching in a carbonate solution 5 minutes after discharge from the furnace, uranium extractions of about 80 per cent were obtained as shown in Test 5, Table 8. If the roasted ore was held for 24 hours before leaching the uranium extractions drop to about 68 per cent as shown by Test 6. It was believed that the rate of cooling the hot calcines after discharge from the roaster had a major effect on the subsequent extraction of uranium, and a series of tests were undertaken to evaluate this variable. This series of tests showed that the faster the rate of cooling the more effective was the carbonate leach for the extraction of uranium. The slower the samples were cooled and the longer the time that the hot calcines were allowed to cool naturally before some form of rapid cooling was started, the lower the uranium extractions.

The best result in arresting aging was obtained by a rapid cooling of the hot sinter on a cold steel plate. Calcines were discharged on a large steel plate at 0 minutes and 5 minutes after removal from the furnace. It required from 12 to 15 minutes for the calcines to reach room temperature. As shown in Tests 1 and 2 in Table 8, the calcines cooled on the steel plate immediately after discharge gave uranium extractions of 85 per cent whether they were leached immediately or were allowed to stand for 24 hours before leaching. This stability

TABLE 8. THE EFFECT OF RATE OF COOLING ON THE EXTRACTIONS OF URANIUM FROM ROASTED CALCINES OF WILD STEER ORE C-7(1)

Test No.	Description	Quench Time Interval(2)	Cooling Time Interval(3)	Aging Time Interval(4)	Uranium Extraction, Per Cent
1	Quenched on steel plate	0 min.	12 min.	15 min.	85
2	"	0 min.	12 min.	24 hrs.	85
3	"	5 min.	15 min.	15 min.	84
4	"	5 min.	15 min.	24 hrs.	79
5	Standard quench test	5 min.	-	5 min.	80
6	Cooled naturally in air	no quench	-	24 hrs.	68
7	Cooled with dry ice	no quench	20 min.	24 min.	64
8	Cooled slowly in furnace with excess air	no quench	2 hrs. 20 min.	3 hrs. 40 min.	6
9	"	no quench	2 hrs. 50 min.	2 hrs. 55 min.	5
10	Cooled slowly in furnace with N_2 atmosphere	no quench	4 hrs. 50 min.	24 hrs.	7
11	"	no quench	5 hrs.	5 hrs.	8

(1) Test conditions were: roasting temperatures 1550 to 1560°F., heating rates 7 to 8°F. per minute, roasting time 15 minutes, air-flow 0.33 c.f.m., leaching solution 3 per cent sodium carbonate, leaching time 30 minutes, leaching temperature 190°F. and pulp density 20 per cent.
(2) The interval of time between discharge from furnace and quenching.
(3) The interval of time between discharge from furnace and arrival at room temperature.
(4) The interval of time between discharge from furnace and start of leaching operation.

was not apparent with calcines that were cooled on the steel plate 5 minutes after discharge from the furnace. Such a procedure, as shown by Test 4, resulted in a decrease of about 5 per cent in the uranium extractions on samples aged for 24 hours. From these data it is apparent that the samples quenched immediately on the cold steel plate showed little aging, indicating that, as in the case of liquid quenching, the cooling rate is an important factor in the aging of calcines.

One sample was cooled by stirring it in a container that was immersed in dry ice. Because of the low rate of heat transfer, it required 20 minutes to bring the sample to room temperature. This rate of cooling was not rapid enough to prevent aging and the uranium extraction was 64 per cent, as shown in Test 7, which is comparable with the extractions obtained from samples that were allowed to cool and age naturally for the same length of time before leaching.

In contrast to rapid cooling, several samples were slow-cooled in the furnace. One test was made with excess air flowing continuously over the charge and with constant rabbling; another, with a nitrogen atmosphere and no rabbling. As shown in Table 8, Tests 8 through 11, the resulting extractions of uranium were only about 5 per cent, both from samples leached as soon as the charges reached room temperature and from samples leached 24 hours later.

The Effect of Roasting Temperature and Heating Gradient

The results of experimental work, shown in Figure 8, indicate that the more rapidly a sample is raised to the desired roasting temperature the higher the uranium extraction and the less the effect of aging. They also show that the optimum uranium extractions correspond to a higher roasting temperature with the more rapid heating rate. The data indicate that the heating rate and optimum roasting temperature are dependent variables.

With a heating rate of 12°F. per minute the optimum roasting temperature was between 1570 and 1590°F. and the standard quenching and leaching procedure gave uranium extraction of 80 per cent. When samples were allowed to stand for 30 minutes before leaching the uranium extraction was decreased by about 7 per cent.

With a heating rate of 2°F. per minute the optimum roasting temperature was between 1520 and 1540°F. and the standard quenching and leaching procedure gave uranium extraction of about 72 per cent. When samples roasted in this manner were allowed to stand for 30 minutes before leaching, the uranium extractions were 15 to 20 per cent lower.

Samples roasted with a heating rate of 6°F. per minute gave results between those discussed for heating rates of 12 and 2°F. per minute. Other test data indicate that when samples were roasted at temperatures below the optimum the loss in uranium extraction because of aging became greater. For example, a sample that was roasted under less

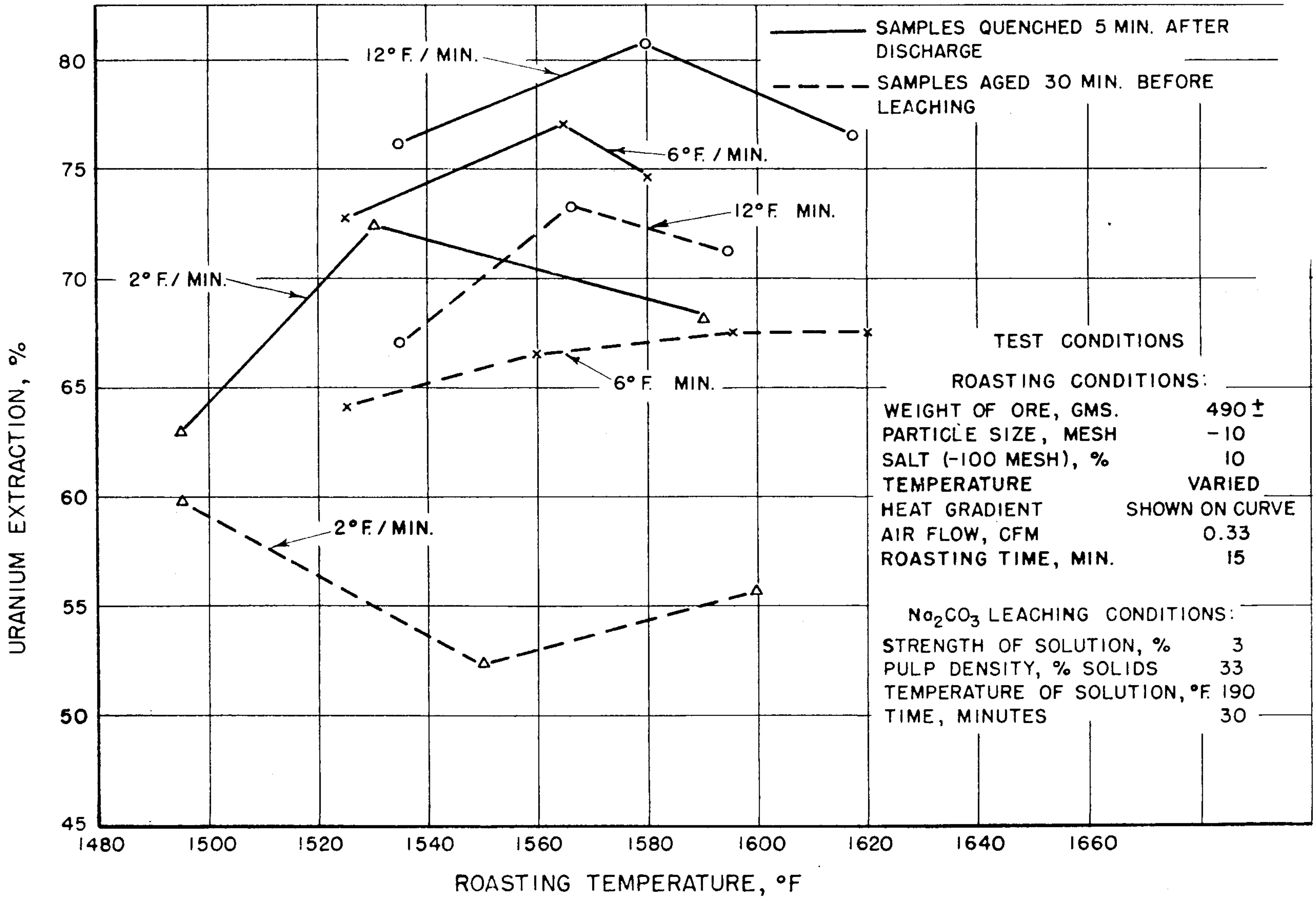

FIGURE 8. EFFECT OF VARYING ROASTING TEMPERATURE AND HEAT GRADIENT ON EXTRACTION OF URANIUM FROM WILD STEER ORE C-7

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than optimum condition may with standard quenching and leaching conditions give uranium extraction of 73 per cent. If, however, this sample is allowed to stand for 30 minutes before leaching the extraction would be reduced to 55 per cent or less.

The Effect of Roasting Time

The length of time that the ore was held at the final roasting temperature had only a slight effect on the ultimate solubility of the uranium within the limits of 0 to 30 minutes. Holding times beyond 30 minutes produced overroasting and gave correspondingly decreased uranium solubility. A roasting time of 15 minutes gave somewhat better solubilities and the best reproducibility from one test to another and was chosen as standard for all subsequent tests.

The length of time a sample was held at the final roasting temperature, within the range of the periods investigated, had no apparent effect on aging. Roasted samples that were allowed to stand for 30 minutes or 24 hours before leaching showed essentially the same decrease in uranium extraction when compared with the extractions obtained from similar samples that had been given the standard quench and leach.

The Effect of Time of Aging

A series of tests were made to determine the effect of the time interval between roasting and leaching on the uranium extraction.

The data shown in Figure 9 indicate that the maximum effect of aging occurred about 15 minutes after the sample was removed from the furnace. The samples that were chilled or "quenched" on a steel plate immediately after they were removed from the furnace gave extractions of 85 per cent of the uranium. Roasted samples that received the standard treatment of being allowed to cool for 5 minutes and were then quenched and leached in the carbonate solutions gave extractions of about 80 per cent. Roasted samples that were held for 15 minutes before leaching gave extractions of about 60 per cent, indicating the maximum effect of aging. Increasing the holding time beyond 15 minutes decreased the effect of aging and the uranium extraction after 30 minutes was about 70 per cent. Holding the roasted samples for still longer periods before leaching slowly increased the effect of aging until after 96 hours the uranium extraction was 67 per cent. This latter extraction, however, was still above the minimum which was obtained after an aging period of 15 minutes.

The Effect of Moisture in the Air During Roasting

Table 9 gives the results of a series of tests which was made with Wild Steer ore to determine the relative effects of wet and dry air during roasting.

The samples roasted with dry air gave uranium extraction of 74 per cent by the standard leaching procedure and an extraction of 70 per cent after aging for 30 minutes.

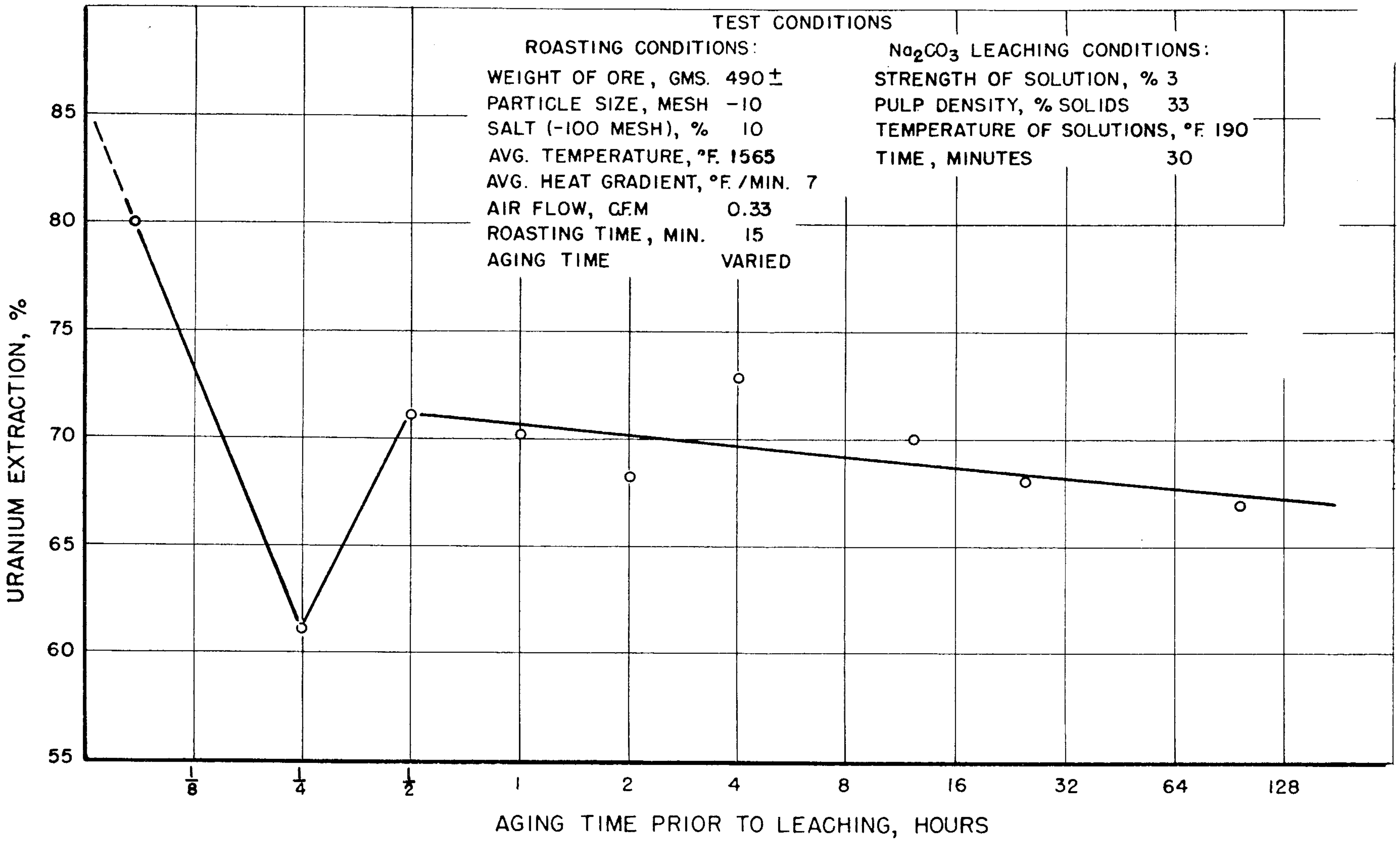

FIGURE 9. EFFECT OF AGING TIME PRIOR TO LEACHING ON EXTRACTION OF URANIUM FROM WILD STEER ORE C-7

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TABLE 9. THE EFFECT OF THE RELATIVE HUMIDITY OF THE AIR ON THE EXTRACTIONS OF URANIUM FROM WILD STEER ORE C-7(1)

Test No.	Air Temperature, °F.	Relative Humidity, Per Cent	Aging Time, Minutes	Extraction of Uranium, Per Cent
1	80	0	5	74
2	80	0	30	70
3	120	94	5	58
4	120	94	30	49

(1) Test conditions: Same as Table 8, page 62.

In the tests with wet air, the air contained 51 grains of water per cubic foot(1) and the uranium extraction by standard procedure was 58 per cent. After aging for 30 minutes, this extraction dropped to 49 per cent.

In addition to the increased extraction the dry air seemed to produce the more stable calcine. However, in most tests on this project the normal air used had a relative humidity of about 7 per cent at 80°F. When the roasting and leaching tests were carried out under the standardized conditions, uranium extractions of 80 per cent or more were obtained. Hence, a small amount of moisture in the air to the furnace was not harmful and may be a benefit.

Leaching Tests on Aged Samples With Various Solutes

To determine the possibility of increasing the extraction from aged calcines, a number of small-scale tests were made using solutes other than 3 per cent sodium carbonate. Samples were aged for 24 hours prior to leaching. Reagents tried included:

1. 3 per cent $NaHCO_3$
2. 3 per cent $(NH_4)_2CO_3$
3. Distilled water
4. 1.5 per cent Na_2CO_3 plus 1.5 per cent $NaHCO_3$
5. 3 per cent Na_2CO_3 plus 5 per cent NaCl
6. 3 per cent Na_2CO_3 plus 5 per cent Na_2O_2

(1) 94 per cent relative humidity at 120°F.

7. 3 per cent Na_2CO_3 plus Cl_2 gas

8. 3 per cent Na_2CO_3 plus SO_2 gas

9. 3 per cent Na_2CO_3 plus CO_2 gas

10. 5 per cent NaCN

11. 3 per cent Na_2CO_3 plus Aerosol 85

The results of these tests were negative except for $(NH_4)_2CO_3$, which was the only reagent that gave a higher extraction of uranium from the aged calcine than Na_2CO_3. Subsequent large-scale tests indicated that $(NH_4)_2CO_3$ was equal to Na_2CO_3 in leaching efficiency on immediate-quench samples and about 7 per cent better on the aged samples.

Miscellaneous Observations

Measurements of the pH, during leaching, of different pulps from Wild Steer ore showed no significant change due to various roasting and aging conditions. Distilled water and 3 per cent carbonate solutions were employed in pulping for pH measurements. No significant correlation of pH with uranium extraction was possible regardless of whether the ore was leached raw, standard leached, aged and leached, or quenched on a steel plate prior to leaching.

The addition of 0.66 per cent of V_2O_5 to Wild Steer ore in a standard test produced a stable non-aging calcine. The extractions of uranium after the calcine was aged for 30 minutes was 80 per cent or

equal to that obtained from a standard quench on ore roasted with or without added vanadium. Without the addition of V_2O_5, aging lowered the extraction of uranium from 80 per cent to 70 per cent.

Theoretical Concept of Roasting and Aging

A theoretical concept of the physical and chemical changes which might occur during roasting and aging of carnotite has been developed as a result of the investigations on Wild Steer ore. This concept is best introduced with the aid of the idealized curves shown in Figure 10. The values in this figure apply to any normal low-lime carnotite ore in which the ratio of U to V_2O_5 is about 1 to 10. It is also assumed that the ore has been raised to the desired roasting temperature at a rate of about 8°F. per minute and held at that temperature for 30 minutes. In Figure 10, the uranium and vanadium extractions, as determined by the soda-soluble analytical method, are plotted against roasting temperature.

Referring to the uranium curve (solid line), extractions of about 95 per cent were obtained for roasting temperatures up to about 570°F. Beyond this temperature the uranium extractions decreased rapidly until a temperature of about 1110°F. was reached, at which point extractions of only 15 per cent were obtained. As the roasting temperature was raised above 1110°F. the uranium extractions increased and at roasting temperatures of about 1570°F. the extraction again reached

STANDARD CONDITIONS

ROAST:

HOLDING TIME, MIN. — 30
HEAT GRADIENT, °F./MIN. — 8 TO 10

LEACH: 3% CARBONATE SOLUTION

WT. SAMPLE, GMS. — 10
VOLUME SOLUTION, ML. — 1000
TIME OF AGITATION, MIN. — 60
TEMP. SOLUTION, °F. — 200

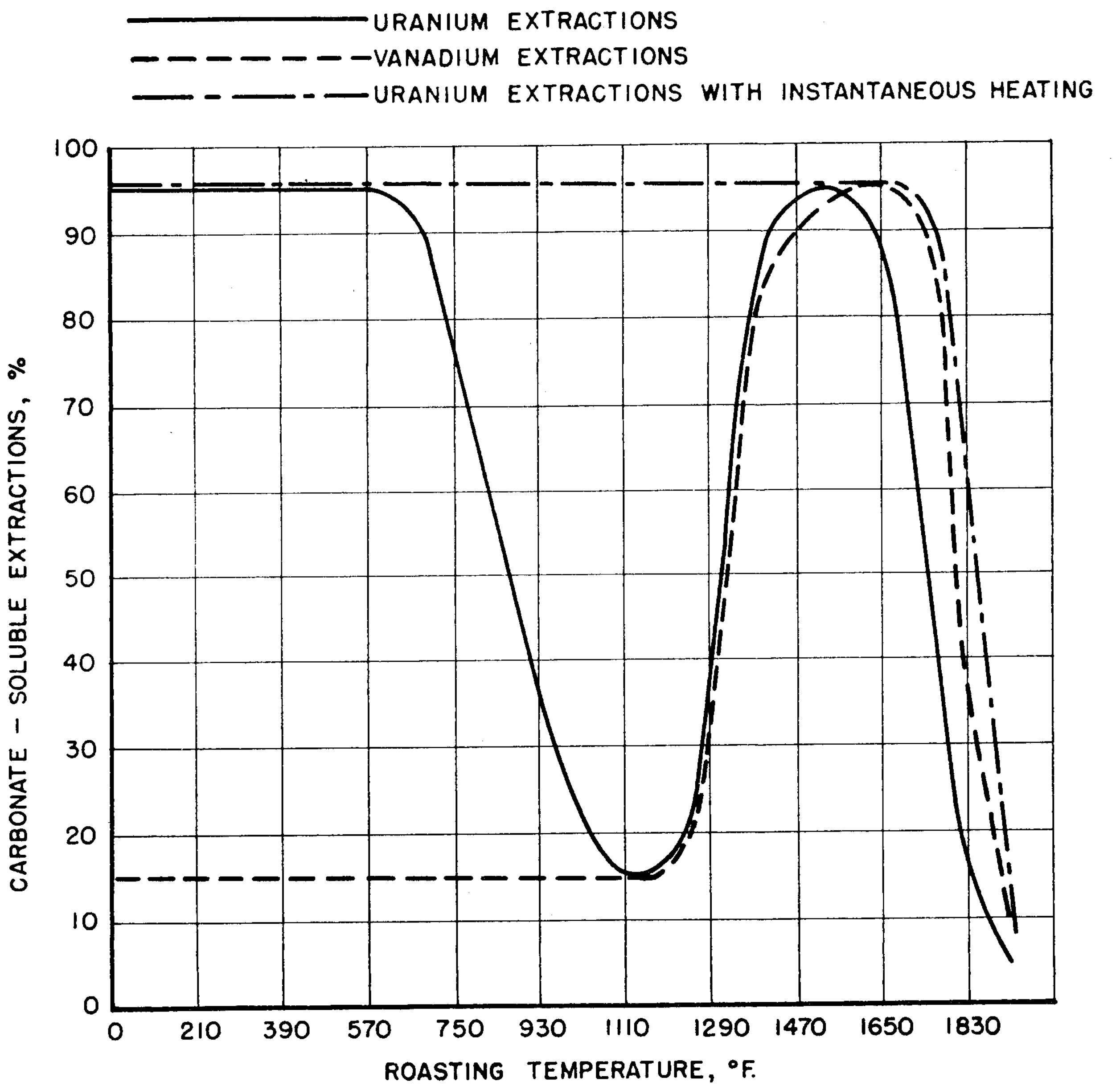

FIGURE 10. IDEALIZED CURVE SHOWING VARIATIONS IN EXTRACTIONS OF URANIUM AND VANADIUM WITH ROASTING TEMPERATURE

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95 per cent. At roasting temperatures above 1560°F. the extractions of uranium decreased rapidly.

Referring to the vanadium curve, a roasting temperature of about 1110°F. was reached before more than 15 per cent of the vanadium became soda soluble. Above this temperature the vanadium extractions were similar to those obtained for uranium with the maximum extraction being obtained at a slightly higher temperature of 1650°F.

To explain these results a theory has been conceived as to the alterations that the minerals containing uranium and vanadium undergo during a salt-roasting operation. It is assumed that uranium is present in the ore primarily as carnotite or tyuyamunite and vanadium is present not only in these minerals but also as vanadium oxides. The uranium and vanadium in carnotite are highly soluble in hot carbonate solutions, but the vanadium in the oxides is only slightly soluble. As the ore is heated to about 750°F. the original uranium minerals start to break down and form an insoluble uranium compound. At this temperature practically all of the uranium becomes insoluble and only about 15 per cent can be extracted by the subsequent carbonate leach. The vanadium minerals seem to remain unaffected. This primary alteration, caused by heating, is assumed to produce a carbonate-insoluble Phase X.

However, as the roasting temperature is increased from 750 to 1560°F., the percentage of uranium that may be extracted increases. For example, the soda-soluble uranium extraction after a 1110°F. roast

was about 15 per cent of the uranium and after a 1560°F. roast the soda-soluble extraction of uranium reached an optimum of 95 per cent.

At 1110°F. a reaction with sodium chloride began which converted the vanadium to a soluble sodium vanadate, such as $NaVO_3$. At this temperature the uranium mineral is evidently soluble in this sodium vanadate because the solubility of the uranium by the subsequent carbonate leach increased as the amount of sodium vanadate present increased. If the amount of V_2O_5 in Wild Steer Ore was increased, the uranium solubility after roasting increased slightly. The conversion of the vanadium to sodium vanadate and the concommitant solubilization of the uranium is assumed to be the result of the formation of a soluble mineral, Phase Y. This conversion reaches a maximum at about 1560°F.

When the ore is roasted above 1560°F. the soluble Phase Y is converted to an insoluble Phase Z which is thought to be due to a change in the sodium vanadate which in turn results in a decrease in the solubility of the uranium. A roasting temperature of 1700°F. resulted in an uranium extraction of only 14 per cent, possibly because of a conversion of the sodium vanadate to complex calcium vanadates, calcium-vanadium silicates, or similar insoluble refractory minerals. The uranium may also become tied up as a silicate and the solubility of both metals decreases rapidly as the roasting temperature increases beyond the optimum.

X-ray diffraction data from synthetic ores showed that Phase X was not sodium diuranate as is frequently suggested in the literature. Regardless of the nature of the starting ore, it has been impossible to detect sodium diuranate in the roasted calcine. It is believed that the soluble Phase Y is a soluble vanadium-uranium compound rather than $Na_4U_2O_7$.

A series of tests on a synthetic ore in which the roasted calcine was re-roasted at various temperatures proved the reversibility of the reaction in the temperature range between 1200 and 1500°F. The extractions of uranium as shown on the temperature curve could be reproduced whether the calcines were roasted at the normal roasting temperature (1560°F.) first and then re-roasted at a lower temperature (1110°F.) or were roasted at the lower temperature initially. Final extractions of uranium were approximately equal because the final roasting temperature was the controlling factor and the reaction was reversible, providing the optimum temperature was not exceeded, in which case, irreversible Phase Z would be formed.

If Phase Y results from the solubility of the uranium mineral in sodium vanadate, then, rapid quenching, to give high solubilities of uranium, could be employed to freeze Phase Y and prevent the uranium from leaving the system. The beneficial effect of quenching may be explained as a "freezing" of Phase Y with a minimum of reversion to the insoluble Phase X. Aging is the breakdown of Phase Y to Phase X. Quenching arrests this action.

Theoretically, there is no reason why Phase X must be formed before Phase Y. If it were possible to heat an ore from 0 to 1560°F., instantaneously, it is conceivable that the original uranium minerals would go directly into solution in the sodium vanadate, without the formation of an insoluble Phase X. This condition is represented in Figure 10 by the dot-dash line for uranium extraction with instantaneous heating. This concept is supported by the fact that rapid heating rates in the temperature range of 1110° to 1560°F. improved the uranium extractions, presumably, by limiting the amount of Phase X that is formed.

Heating rates of from 2 to 8°F. per minute appear to be those that permit the formation of an appreciable amount of Phase X which is subject to greater aging effects. A heating rate of 12°F. per minute seemed to reduce the amount of Phase X formed and promoted the formation of a more stable Phase Y, as indicated by the slightly higher uranium extractions obtained with standard leaching procedures and the reduced effects of aging.

The theory presented in the preceding paragraphs has been postulated from the results of experimental work on aging. Further work based on X-ray diffraction data and chemical analyses should be carried out to identify the phases referrred to as X, Y, and Z. Experimental work should also be undertaken on the reversibility of these phases.

Precipitation of Uranium From Carbonate Solutions

Introduction

At the Monticello plant, the precipitation of uranium as artificial carnotite, and vanadium as V_2O_5, is effected by neutralizing the pregnant solution with sulphuric acid. By regulating the amount of sulphuric acid, it is possible to precipitate, first, virtually all of the uranium as artificial carnotite, and then, after filtration of the double salt, to precipitate the remaining vanadium almost completely as V_2O_5. It has been the practice at the plant to gauge the amounts of acid required for each of these steps by back-titrating the solution with standard NaOH to the phenolphthalein end-point.

This section of the report represents the data and conclusions of work undertaken to evaluate the possibility of employing pH measurements as a more positive method of controlling the precipitation.

Preliminary Precipitation Experiments on a Synthetic Solution

The synthetic solution employed, for preliminary precipitation tests, was made from sodium diuranate, the fusion product of V_2O_5 and Na_2CO_3, and excess Na_2CO_3. It contained, by analyses, 2.445 grams per liter of uranium and 25.35 grams per liter of V_2O_5. Also present in the synthetic solution were 30 grams per liter of total Na_2CO_3 and about 2 grams per liter of chloride ion. Silicates and aluminates were absent.

Figure 11 is a qualitative expression of the results obtained when one liter of this solution was titrated with H_2SO_4 by adding the acid in small increments. After each addition, two minutes was allowed for the acid to react.

A faint yellow turbidity occurred at about pH 7.8 and shortly thereafter a heavy precipitate developed. In the range in which the precipitate remained yellow, there was a definite tendency for the pH values to rise during the two-minute waiting periods.

The extent of the pH rise within two minutes is shown by the shaded area on the curve. At a pH value of about 5.6, the solution and precipitate changed from a canary yellow to an orange color. It is believed that the formation of pentavanadate accounted for the change in color. At a pH of 3.2 the precipitate turned a dark tan color and at a pH of 2.0 the precipitation of red V_2O_5 was apparent.

In order to gain some idea of the extent of the upward drift of the pH value which occurred in the precipitation range, an additional qualitative test was made in which 250 ml. of the solution was titrated with 9.56 normal H_2SO_4 at 194°F. In this test the intervals of time between the addition of the increments of acid were increased to from 5 to 10 minutes. Figure 12 depicts the results graphically. In the figure the upward drift of the pH values during the intervals is shown by the dotted lines. The numbers beside the dotted lines indicate the time, in minutes, during which the drift occurred. In none of the

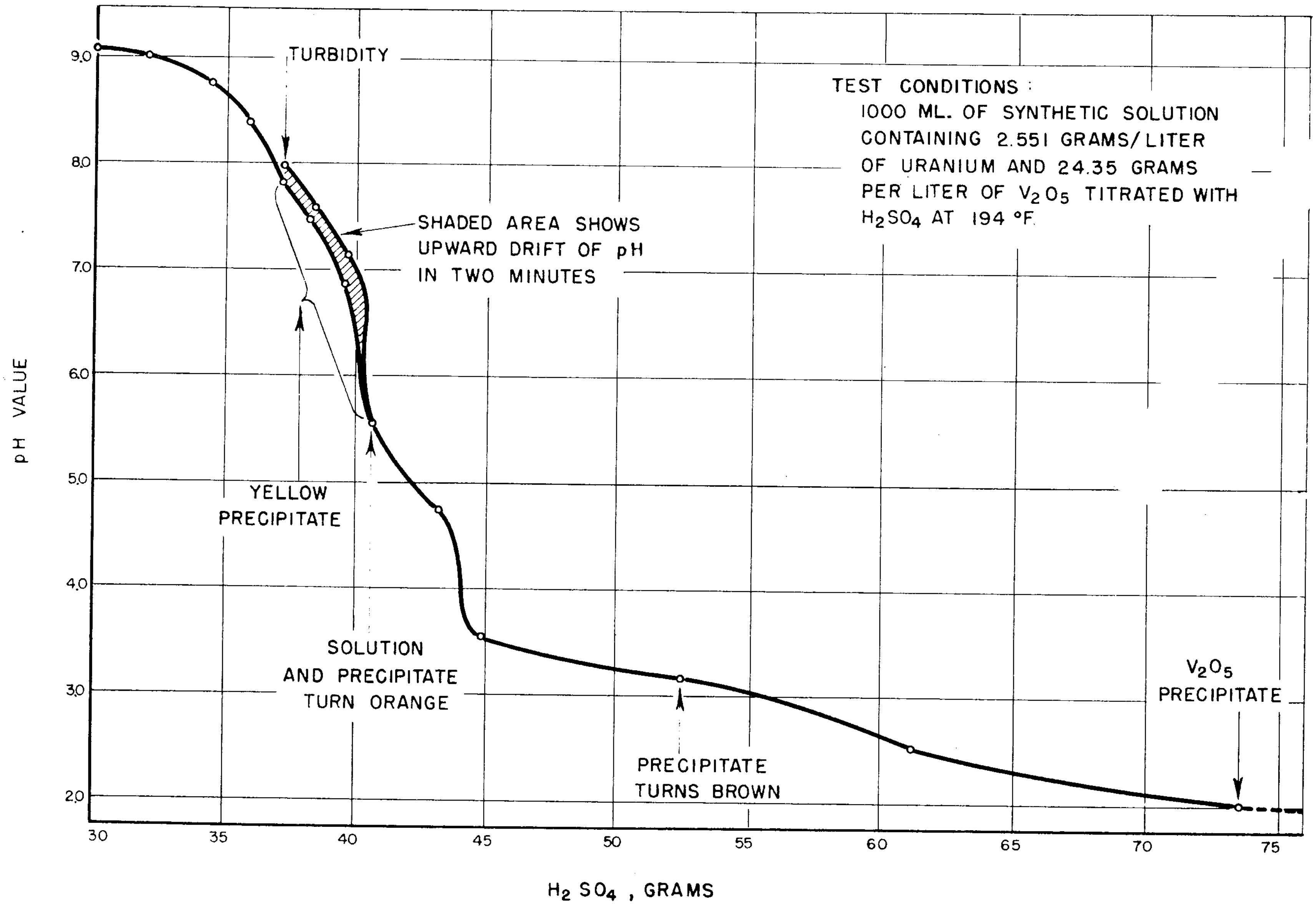

FIGURE 11. TITRATION OF SYNTHETIC SOLUTION WITH H_2SO_4 AT 194 °F.

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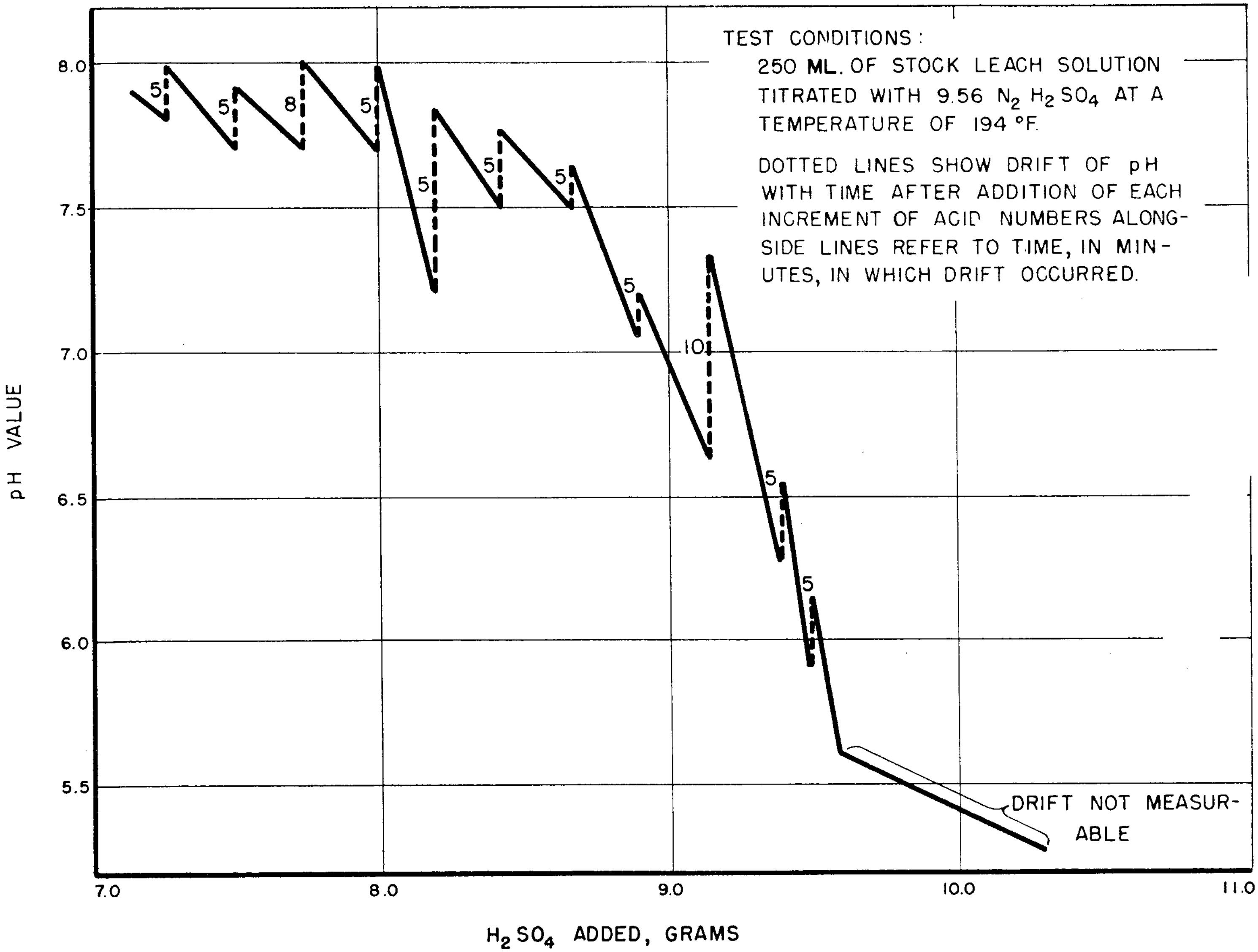

FIGURE 12. DRIFT OF pH DURING TITRATION, AT 194 °F., OF STOCK LEACH SOLUTION WITH H_2SO_4.

0-10,091

observed cases was the upward drift halted, even after 10 minutes. The slow re adjustment was believed to be due to the combined effect of the thermal decomposition of sodium bicarbonate and the precipitation of the artificial carnotite.

A series of precipitation tests was made in which the solutions were held for 30 minutes at 194°F. after the addition of the acid. The conditions and results of this series of tests are shown in Table 11.

In no case was complete precipitation of uranium obtained, even though more than enough acid was added to combine with the total sodium carbonate present and the pH values were in the range in which complete precipitation should occur. The occurrence of additional precipitation in the filtrates after standing overnight at room temperature suggested that the precipitation of uranium even under proper conditions of acidity was a slow process and that the 30 minutes' heating at 194°C. after addition of the acid was not sufficiently long to permit the system to come to equilibrium. Failure of the uranium to precipitate completely may be due to any one or a combination of the following:

1. The slow dissociation of $Na_4UO_2(CO_3)_3$.
2. The slow dissociation of the polyvanadic complex from which the V_2O_5 must be liberated to form artificial carnotite.
3. The tendency of the artificial carnotite to form supersaturated solutions or to be colloidal in nature when first formed.

TABLE 11. RESULTS OF PRECIPITATION TESTS ON SYNTHETIC SOLUTIONS(1)

Test No.	Volume of Solution, ml.	pH Values: Initial(2) at 194°F.	pH Values: After 30 Minutes at 194°F.(3)	pH Values: At 77°F.(4)	Uranium Precipitated, Per Cent	Remarks
9	250	6.6	7.5	7.6	72	Delayed precipitation occurred in filtrates
12	250	5.2	5.6	5.6	50	Ditto
13	250	4.5	4.5	3.6	52	Ditto
18	250	3.9	3.9	3.3	76	Ditto

(1) Solution contained 2.45 grams/liter of U, 25.4 grams/liter of V_2O_5; 30 grams/liter of Na_2CO_3.

(2) Taken within 2 minutes after acid addition.

(3) Heating continued 30 minutes after acid addition.

(4) These pH values were measured on the filtrates.

Precipitation of Uranium from a Stock Solution

Preparation of a Stock Solution. In order to obtain a solution with which to study the effect of hydrogen ion concentration on the precipitation of uranium, representative samples of Wild Steer ore containing 0.34 per cent of uranium were roasted with 10 per cent of salt at 1520°F. in a single-hearth furnace and leached with a hot 3 per cent solution of sodium carbonate. Since it was desired to prepare a solution which would assay 2.5 grams per liter of uranium, the leached ore was filtered and the resulting filtrate was again used to leach additional roasted ore. In this manner, ten liters of solution for precipitation studies were prepared. The solution contained 2.51 grams of uranium and 33.57 grams of vanadium pentoxide per liter.

Experimental Precipitation Procedure. In all the precipitation experiments presented in this report, 250 ml. of the leach solutions containing uranium and vanadium were heated to 194°F. and stirred mechanically, and sulphuric acid was slowly added to the leach solutions by means of a burette. As the acid was added to the solution, the pH values of the solution were recorded continuously. During the course of the titration of the solutions with sulphuric acid, gas evolution, turbidity, appearance of the precipitate, and stability of pH values were noted.

In some of the tests, the solutions were heated to 194°F. and agitated for varying times, after which the pH value was determined.

After the precipitates were formed they were filtered and the pH value of the filtrate was again ascertained. The filtrates were assayed for uranium and the recovery of uranium by precipitation was calculated by difference. In a few of the tests the unwashed precipitates were dissolved in dilute sulphuric acid and analyzed for vanadium and uranium.

Effect of Time on the Completeness of Uranium Precipitation. Because the precipitation of uranium from the synthetic leach solutions indicated that incomplete precipitation and post-precipitation occurred in the filtrate after the solutions were filtered, a series of four tests was made to determine whether heating the solutions at 194°F. for various times would result in a more complete precipitation of uranium.

The results of this series of tests are presented in Table 12 which shows that complete precipitation of the uranium in solution was obtained when the solutions were acidified to a pH of 6.2 and heated at 194°F. for two or four hours. Only 92 per cent of the uranium was precipitated in one hour of heating and only 80 per cent when the solution was allowed to stand overnight at room temperature.

Under the condition of these experiments, it appears that the time required to attain equilibrium conditions and to precipitate the uranium completely was between two and four hours at 194°F. Since there was a rise in pH from 6.2 to 7.7 during the precipitation of uranium the higher pH value might be used as an indication to show when the uranium is completely precipitated.

TABLE 12. EFFECT OF TIME ON THE COMPLETENESS OF URANIUM PRECIPITATION

Test No.	H_2SO_4 Added, Grams	pH Values Initial 194°F.	pH Values Equilibrium 194°F.	pH Values Filtrates 77°F.	Additional Heating Time, Hrs.	Uranium Precipitated, Per Cent
19-2	9.50	6.2	7.2	7.7	4	100
19-6	9.50	6.0	7.3	7.6	2	100
21	9.50	6.2	7.2	7.5	1	92
26-6	9.50	6.2	7.2	N.D.	0	80

Determination of Length of Time for Solution to Reach Equilibrium. Since previous precipitation studies indicated that the pH value of the acidulated solutions, upon heating, rose from the initial pH values, a series of experiments was made to determine the length of heating time required for the solutions to reach a constant pH value.

Figure 13 illustrates the rise in the pH value of the solutions as the heating period was increased. From the graph it may be seen that about 105 minutes of heating at 194°F. was required for the solutions to reach constant pH values. Analysis of the filtrates showed that all the uranium in the solutions was precipitated except in the test in which the initial pH of the solution was 7.9. The attainment of equilibrium would probably be considerably more rapid in boiling solutions.

Effect of the Hydrogen Ion Concentration on the Completeness of Uranium Precipitation. Several series of tests were made to determine the relationship between the pH value and the extent of the precipitation of uranium. Figure 14 shows the pH values obtained in these tests against the weight of sulphuric acid employed. Three curves are given. The bottom curve shows the pH values within 2 minutes after the addition of the acid; the middle curve those obtained at 194°F. when the upward drift had stopped (2 to 4 hours), and the top curve, those obtained on the filtrates after they were cooled from 194°F. to room temperature.

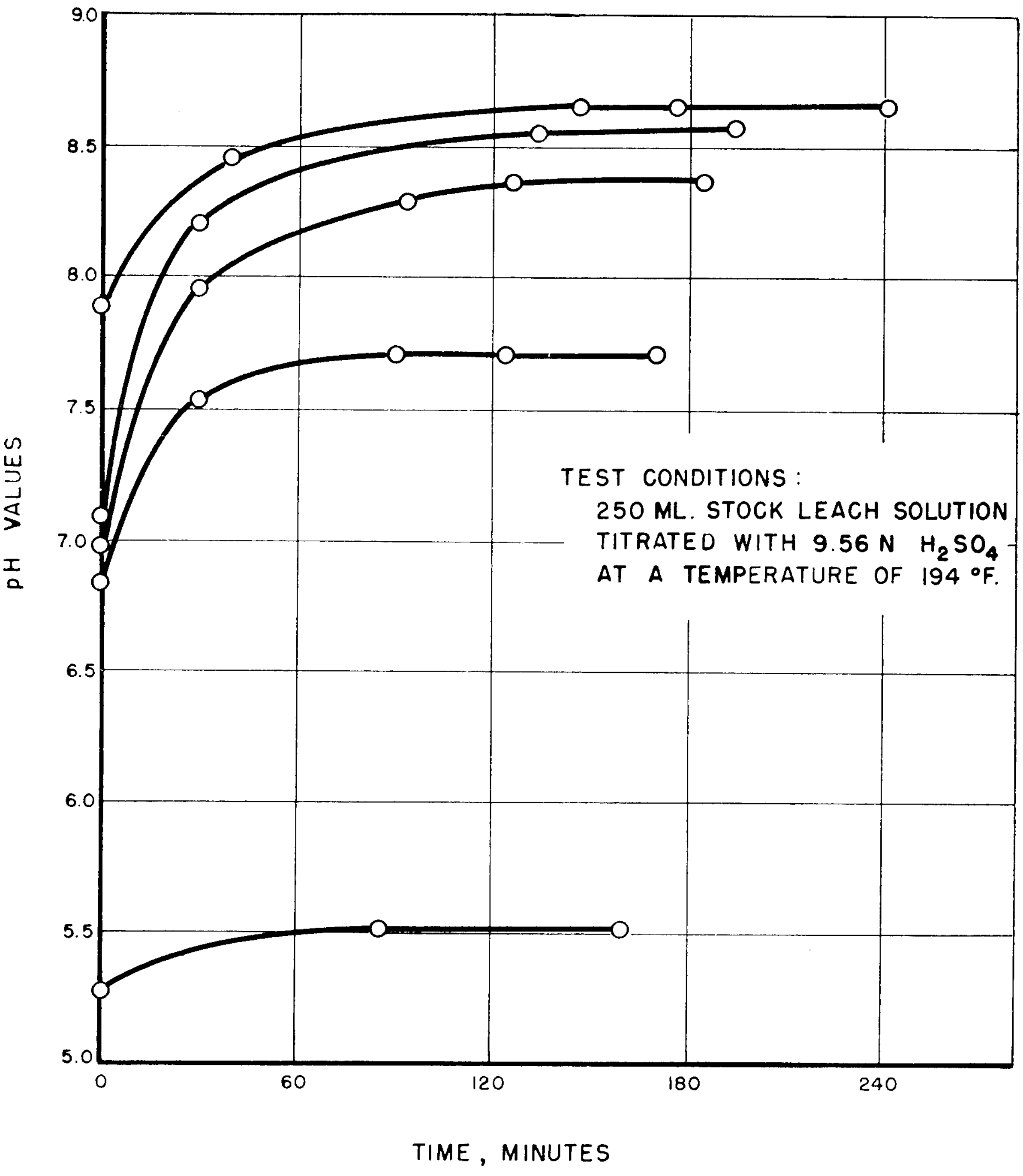

FIGURE 13. DRIFT OF pH WITH TIME AT VARIOUS INITIAL pH VALUES; MEASURED AT 194 °F.

0-10,092

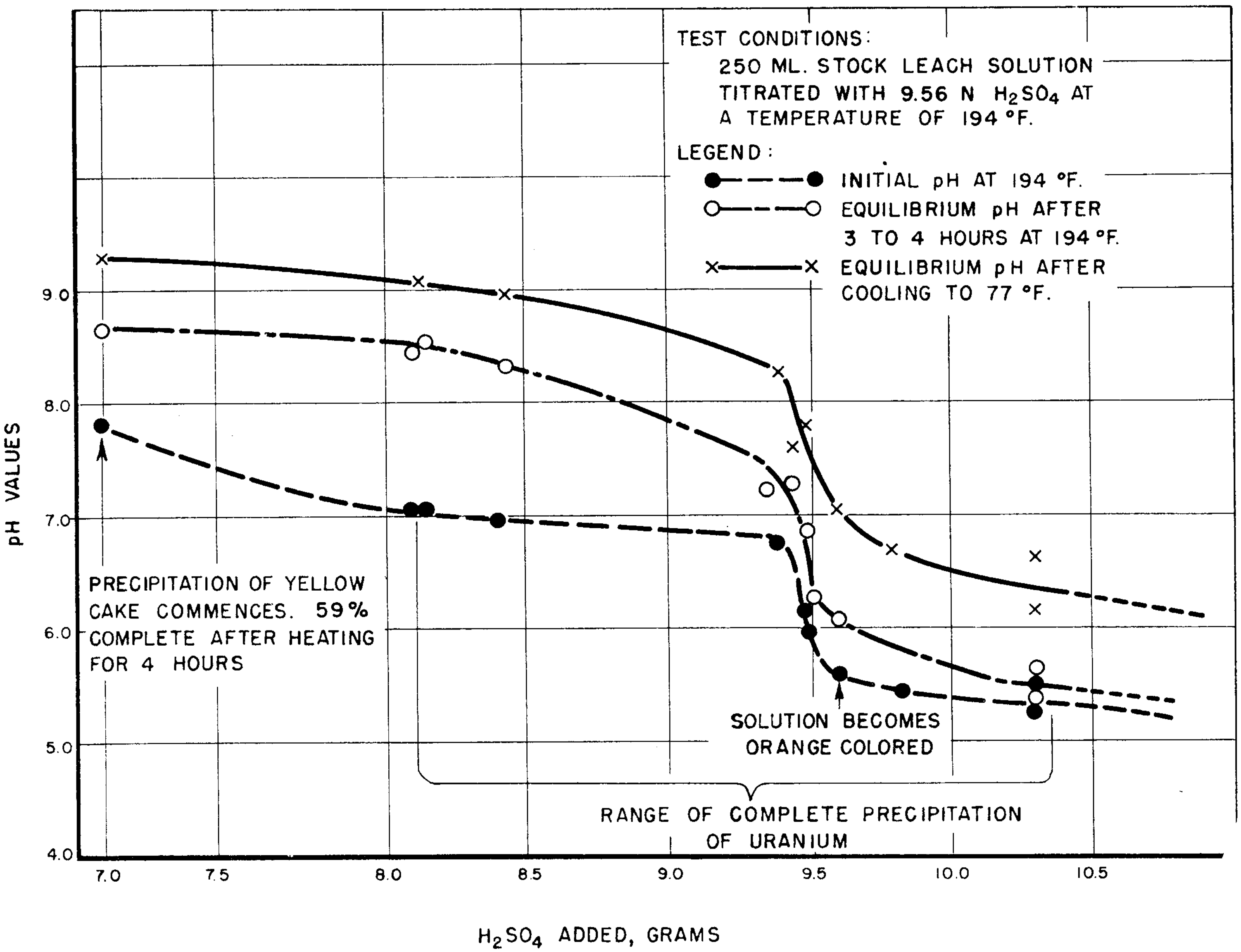

FIGURE 14. EFFECT OF TIME AND TEMPERATURE ON pH DURING TITRATION OF STOC... SOLUTION WITH H_2SO_4 AT 194 °F. AND ADJUSTMENT OF pH TO EQUILIBRIUM.

0-10,093

A faint turbidity developed at an initial pH of 7.9, after 7.0 grams of H_2SO_4 had been added. This amount of acid is close to the stoichiometric amount required to neutralize the total Na_2CO_3 in the sample. With the addition of more acid, the initial pH values declined to about 6.8 when a pronounced inflection in the titration curve occurred. The inflection began just before the point where the solution and precipitate turned an orange color. Before this point was reached the precipitate and solution were canary yellow in color.

The equilibrium pH values shown in the middle curve in Figure 14 were obtained in from 2 to 4 hours of additional heating at 194°F. These equilibrium values were from 0.8 to 1.4 unit higher than the initial values in that range of the curve above the inflection point (approximately pH 6.2). Very little drift occurred in the ranges below the inflection point.

The pH values of the filtrates, at room temperature, were higher than the equilibrium values. This, however, is believed to be due to the effect of temperature.

Table 13 extends the data of Figure 14, by showing the percentage of uranium precipitation obtained in the tests and it will be noted that in all the tests, except 26-1, complete precipitation of uranium occurred.

The range of complete precipitation was from pH 7.1 to 5.2 (initial value at 194°F.); from pH 8.3 to 5.3 (value at equilibrium at 194°F.) and from pH 9.2 to 6.1 (value obtained on the filtrates of

TABLE 13. COMPLETENESS OF URANIUM PRECIPITATION AT VARIOUS pH VALUES

Test No.	pH Values[1] Initial at 194°F.	At Equilibrium at 194°F.	Filtrate, Room Temperature, 77°F.	Uranium Precipitated, Per Cent[2]	Color of Precipitate
26-1	7.9	8.6	9.4	59	Canary Yellow
26-2	7.1	8.3	9.2	100	"
19-1	7.1	8.6	9.2	100	"
26-4	6.9	7.7	8.3	100	"
19-2	6.2	7.2	7.7	100	"
19-6	6.0	7.3	7.7	100	"
19-5	5.6	6.1	6.9	100	Orange tan
26-5	5.3	5.6	6.2	100	"
19-3	5.2	5.3	6.1	100	"

(1) See section on "Experimental Precipitation Procedure", page 84 of this report for further significance of pH values.

(2) Based on analysis of head sample and of filtrate. Confirmed by analysis of precipitates.

equilibrium solutions at 77°F.). It is believed, however, from the difference in appearance of the precipitates and from analytical data later discussed, that the precipitates differed widely in composition. The precipitates formed at the higher pH values apparently contained considerably less vanadium than those formed in Tests 19-5, 26-5, and 19-3 at lower pH values.

The data in Table 13 also suggest that the precipitation by reducing the initial pH values to about 7.1 as in Tests 26-2 and 19-1 might be critical, since the pH conditions of this test are not very different from those of Test 26-1 in which only 59 per cent of the uranium was precipitated. The rate of acid addition also influenced the initial pH significantly as is shown by a comparison of the corresponding acid additions and pH values in Figures 12 and 14.

By reducing the initial pH to 6.2 or lower, in which range the effect of the rate of acid addition within practical limits would only be slight, complete precipitation of uranium would be assured. After the attainment of this pH it would still be important to continue the heating until precipitation was complete.

The length of the heating period can probably be gauged by pH methods. From the data of these tests it appears that in the pH ranges above the inflection region, pH 7 to 8, the precipitation is complete when the pH assumes a constant value. This is probably not true in the pH range below the inflection point in which the drift is small. There

is some basis for believing that a minimum heating period of 2 hours is required to effect complete precipitation in this low range at 194°F., even though pH equilibrium has apparently been reached. This point requires additional test work for confirmation.

<u>Effect of Carbon Dioxide on the Completeness of Uranium Precipitation</u>. The analyses of a few samples indicate that the complete removal of CO_2 from solution was not required for substantially complete uranium precipitation. For example, the filtrate from Test 19-1, in which the precipitation of uranium was complete, contained about 7 per cent of the CO_2 originally present in the carbonate leach liquor.

<u>Composition of the Precipitates Obtained at Various pH Values.</u> As mentioned previously, precipitates obtained in the range above and below the inflection point, about pH 5 to 6, varied in appearance. Those made in the high pH ranges were canary yellow in color, while those in the lower range were orange-tan. It was believed that the difference in color was due to the effect of variations in the vanadium content.

Table 14 shows the $U:V_2O_5$ weight ratio of the precipitates formed at various pH values. The departure of the ratios of U to V_2O_5 from the approximately correct value in artificial carnotite was probably due to the mother liquor retained in the precipitates. It is clear from the table, however, that in Test 19-3, in which the pH at precipitation was 5.2, considerably more vanadium was present in this

TABLE 14. URANIUM AND V_2O_5 RATIO IN PRECIPITATES FORMED AT VARIOUS pH LEVELS

Test No.	pH At Precipitation	Weight Ratio $U:V_2O_5$
19-1	7.1	1.59 : 1
19-2	6.2	1.49 : 1
19-3	5.2	0.69 : 1

precipitate than in those formed at higher pH values. It would be desirable to determine on a larger scale the exact ratios of U to V_2O_5 in precipitates made at various pH values.

The Effect of Temperature on the pH Values. The tests described in this report were run at a temperature of 194°F. because above this temperature the type of glass electrode used in the experiments rapidly deteriorates. It was noted during the tests, however, that temperature differences within certain limits exerted a minor effect on the pH values. At temperatures of about 176°F. the indicated pH values were about 0.2-0.3 of a unit higher than they were at 194°F. No observations were made at boiling temperatures because these were deliberately avoided. It is believed that the entire pH curve would be adjusted upward by about 0.2 of a pH unit if the tests had been run at 176°F. instead of at 194°F. It is also believed that the rate of precipitation of uranium would be lower at 176°F. than it was at 194°F. and that at boiling temperatures the rate would be increased.

Possibilities of Using pH as a Method of Controlling Uranium Precipitation in Plant Practice

As a result of the experimental work on the precipitation of uranium from sodium carbonate solutions with sulphuric acid, it is believed that it is possible to control the acid additions and hence the

precipitation conditions by means of pH measurements. Further experimental work would be required to evaluate all of the influencing variables and prove that it is a feasible commercial method.

The experimental work has shown that the acidified solutions are slow in reaching equilibrium and that the apparent pH varies as a function of temperature and rate of acid addition. However, under any given set of conditions there is a definite inflection point in the pH acid addition curve which corresponds to an initial pH of 6.2. Since this value is well within the range of complete precipitation (pH 7.1 to 5.2) it would appear to offer an easy method of controlling the amount of acid required to reach suitable precipitation conditions. Furthermore, after the correct acid addition has been made as indicated by the inflection point, and the solution is being heated and agitated to aid in precipitation of the yellow cake, there is a definite rise in the pH value of the solution. This rise continues until precipitation is complete, at which time the pH value becomes constant. This characteristic should make it possible to determine correct holding times for the solutions during precipitation, although in plant practice it may be advisable to hold the solution for some empirical length of time after the pH has become constant, in order to allow the precipitated yellow cake sufficient time to agglomerate or crystallize prior to separation, and thus increase the filtering rates.

Some modifications in this procedure may be necessary depending on actual plant conditions of solution temperature, rate of agitation, and chemical composition of pregnant liquor. However, these should be minor factors and can best be evaluated by actual operation in the plant.

Precipitation of Uranium From Ammonium Carbonate Solutions

To study the precipitation of uranium from ammonium carbonate solutions, a pregnant liquor was prepared by leaching roasted Ore C-7 with a 3 per cent ammonium carbonate solution. One liter of this pregnant solution, containing 0.392 gram of uranium and 5.94 grams of vanadium pentoxide, was used to determine whether the uranium could be precipitated as a double salt after the ammonium carbonate was removed by boiling. The removal of the ammonium carbonate lowered the pH of the solution below 7 and resulted in the formation of a yellow precipitate which was filtered, dried, weighed, and assayed. The analysis of this precipitate showed that it contained 45 per cent of uranium and 20 per cent of vanadium pentoxide. The original pregnant liquor contained 0.392 gram of uranium and the final filtrate contained 0.0012 gram of uranium, which indicated a precipitation of 99.7 per cent of the total uranium.

These results indicate that it should be possible to use this method for the recovery of uranium as an artificial carnotite from pregnant ammonium carbonate solutions. If the vanadium can be recovered in a subsequent step, this method of recovering uranium would offer

advantages over the sodium carbonate method now in use, since reagent consumption would be relatively low and plant control would be simplified.

Roasting in a Fluidized Bed

Small-scale tests on individual ores had indicated that it would be advantageous to salt roast the carnotite ores at sizes finer than minus 10 mesh, the lower limit of practical feed size for a hearth-type furnace operating on carnotite ores. Also, maintenance on the hearth-type furnaces has proved to be costly in plant operation. The use of a furnace with a fluidized bed for the salt roasting of the carnotite ores was investigated because if operable such a unit would overcome both the difficulties of feed particle size and of high maintenance cost. The following section of this report covers a preliminary investigation of roasting in a furnace with a fluidized bed.

A small fluidized-bed furnace was constructed, consisting of a 4-inch inside diameter fused quartz tube, 24 inches long, mounted in a vertical position and heated externally by means of a resistance winding. At a depth of 18 inches below the upper end of the quartz tube, a diffusion plate made from K-30 brick was cemented into the tube. The section of this furnace below the diffusion plate served as an air chamber while the section above the plate held the fluidized ore. A discharge tube one inch in diameter extended downward from the diffusion plate, through the air chamber and out the bottom of the furnace.

In actual operation, an ore bed approximately 6 inches in depth was held in a fluid condition using air as a fluidizing medium. Fresh feed was added at the top of the furnace by means of a vibrating feeder, and roasted ore was discharged from the bottom of the unit through a controlled discharge. The residence time in the unit was controlled by regulating the throughput of the ore.

A series of eight tests was carried out, and the results of two tests are as follows:

Test No.	Ore	Type of Test	Uranium Extraction, Per Cent
2	Wild Steer C-7	Batch	83.9
6	Wild Steer C-7	Continuous	79.8

These tests made with Wild Steer Ore C-7 showed promising results and indicated that the fluidized-bed furnace may be suitable as a furnacing unit for the salt roasting of carnotite ores. Temperature ranges of from 1470 to 1520°F. produced the best extractions of uranium. There was no appreciable dust loss during roasting even with 100-mesh ore and relatively high air-flow rates. The salt tended to agglomerate the fines at this temperature and to eliminate dusting. Ten per cent of salt was the standard amount but as little as seven and one-half per cent gave satisfactory results. Pulsating air flow to the furnace prevented the formation of blow holes in the bed and gave smoother operations and

more even temperatures throughout the bed. The use of coke for generating internal heat for roasting the fluidized bed resulted in calcines which showed leach extractions of uranium comparable with those obtained from roasts in which no coke was added and in which external heating was used. Further experimental work is necessary to establish the commercial possibilities of this method of roasting.

Leaching and Precipitation With Recycled Reagents

Cyclic Flowsheet

The process used for recovering uranium and vanadium from the pregnant liquors in the Monticello flowsheet has proved to be highly efficient, yielding recoveries as high as 99 per cent of the uranium and 98 per cent of the vanadium in the form of high-grade products. However, this process entails a high consumption of sodium carbonate and sulphuric acid with a resulting high operating cost. With these factors in mind, the following preliminary experimental work on precipitation was directed toward evaluating a system in which the reagents could be recycled and still give a high recovery of the values in the pregnant liquor.

The process which was investigated in the laboratory is shown in flowsheet form in Figure 15. In this process, uranium is precipitated from solution as a diuranate by adjusting the pH to 11 with sodium hydroxide. If necessary, the sodium carbonate in the solution is first

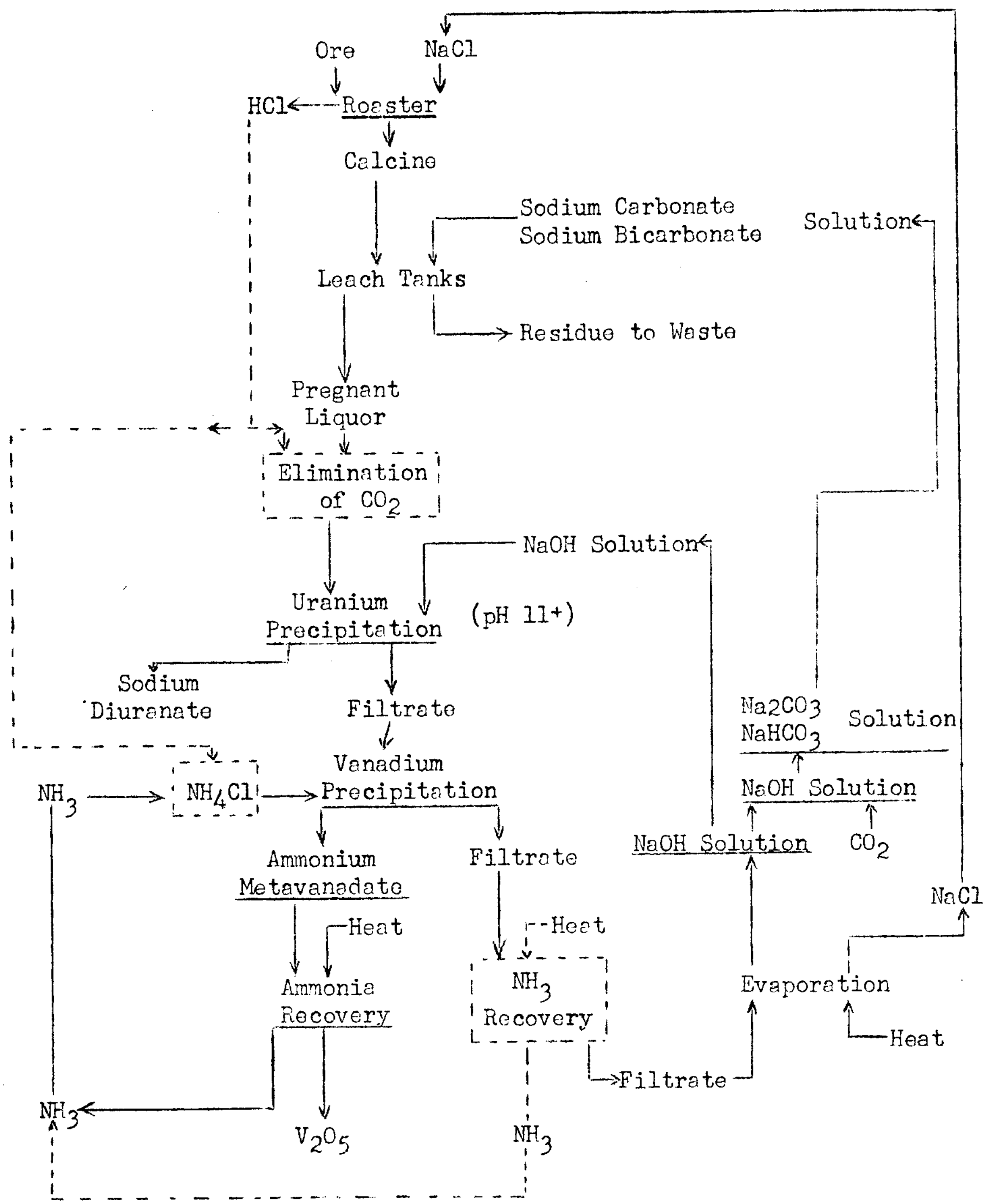

Figure 15. Flowsheet Showing Precipitation With Cyclic Reagents

neutralized with hydrochloric acid obtained from the roaster gases. After the uranium has been removed from the solution, the vanadium is recovered as ammonium metavanadate either by the addition of ammonia gas or ammonium chloride. The remaining filtrate is concentrated by evaporation until a sodium chloride precipitate is obtained for use in the roasting cycle. The remaining solution containing sodium hydroxide is divided into two parts, the first being used for pH adjustment of additional pregnant liquor, while the second portion is converted to a sodium carbonate-sodium bicarbonate solution by passing carbon dioxide obtained from burning coke into the solution. This carbonate solution is then reused as leach liquor.

Such a process would require little or no make-up reagent and should be efficient because any values escaping precipitation would be returned to the leach-liquor circuit.

Precipitation of Diuranate

Several tests have been made to determine the effect of pH and the presence of the carbonate ion on the precipitation of sodium diuranate from alkaline solutions. The results of these tests showed that in the presence of the carbonate ion, in concentrations similar to those of the pregnant liquor in plant practice, pH adjustment with sodium hydroxide was only partially effective in precipitating uranium as sodium diuranate. These data indicate that when the pH was raised to 11.3 with sodium

hydroxide, approximately 25 per cent of the uranium was precipitated when the solution was boiled. If the pH is raised to 12.0 with sodium hydroxide, approximately 50 per cent of the uranium may be recovered as a diuranate precipitate. These diuranate precipitates had a uranium to vanadium ratio of 5.5 to 1.

If the carbonate ion is removed by neutralizing the solution to a pH of 6.3 with HCl and followed by boiling, 65 per cent of the uranium can be precipitated as diuranate after a pH adjustment to 10.8 with sodium hydroxide. If the neutralization of carbonate with HCl is carried out at a pH of 7, the subsequent precipitation of uranium as a diuranate at a pH of 11.0 recovers only 20 per cent of the uranium.

In no case, either with or without carbonate neutralization, was the precipitation of uranium as sodium diuranate more than 65 per cent complete. This would result in a high circulating load of uranium in the plant liquors.

Precipitation of Synthetic Carnotite

Several tests were made in which the pregnant solution was neutralized to a pH in the range of 6.4 to 6.0 with hydrochloric acid, and the uranium precipitated as synthetic sodium carnotite or yellow cake, by boiling. These tests showed that over 98 per cent of the uranium could be precipitated by this method in a product assaying 41 per cent uranium and 22 per cent vanadium.

Precipitation of Ammonium Metavanadate

A series of tests was carried out to explore the feasibility of precipitating vanadium from basic solutions, in the form of ammonium metavanadate, by passing ammonia gas through the solutions.

In these tests a white precipitate was formed at temperatures below 120°F. when the solution was saturated with ammonia gas. Upon standing, the ammonia gas which had been dissolved in the solution was liberated and the precipitate redissolved, indicating that it was soluble in hydroxide solution unless saturated with ammonia. Analysis of this white precipitate showed that it was largely sodium chloride, sodium hydroxide, and sodium silicate. All of the vanadium in this precipitate was in the form of sodium metavanadate, and not as ammonium metavanadate as desired. Apparently, the sodium salts have a low solubility in solutions saturated with ammonia.

The results show that there is little possibility of developing a process for recovering vanadium from plant liquors as ammonium metavanadate by the use of gaseous ammonia.

However, according to Seidel[1] only 0.41 gram of ammonium metavanadate per liter is soluble in a 0.1 normal ammonium chloride solution at 18°C. Therefore, a method for precipitating vanadium from alkaline solutions according to the equation: $NaVO_3 + NH_4CL = NH_4VO_3$

(1) Seidel, Atherton, Solubilities of Inorganic and Metal Organic Compounds, Vol. 1, page 1135, 1940 addition.

+ NaCl might prove feasible. Accordingly, a series of experiments was made to evaluate this method of precipitating vanadium.

The following tabulation illustrates the effect of the ammonium chloride concentrations on the precipitation, at room temperature, of vanadium from pure sodium metavanadate solutions. The same data are presented in the form of a curve in Figure 16.

NH_4Cl Concentration, g/l. Excess(1)	NH_4Cl Concentration, g/l. Total	Filtrate Assay V_2O_5, g/l.	V_2O_5 Precipitated, Per Cent
0.0	14.42	23.2	5.4
5.35	19.77	20.4	16.8
10.70	25.12	15.4	37.1
26.75	41.17	3.9	84.2
53.50	67.92	0.9	96.2
107.00	121.42	0.3	98.8

From these data it may be concluded that at least 98 per cent of the total V_2O_5 in a chemically pure $NaVO_3$ solution can be precipitated by the addition of a stoichometric quantity of ammonium chloride plus an additional quantity of ammonium chloride sufficient to produce a 2 normal ammonium chloride solution.

(1) Excess above the stoichiometric amount required to convert all sodium metavanadate to ammonium metavanadate.

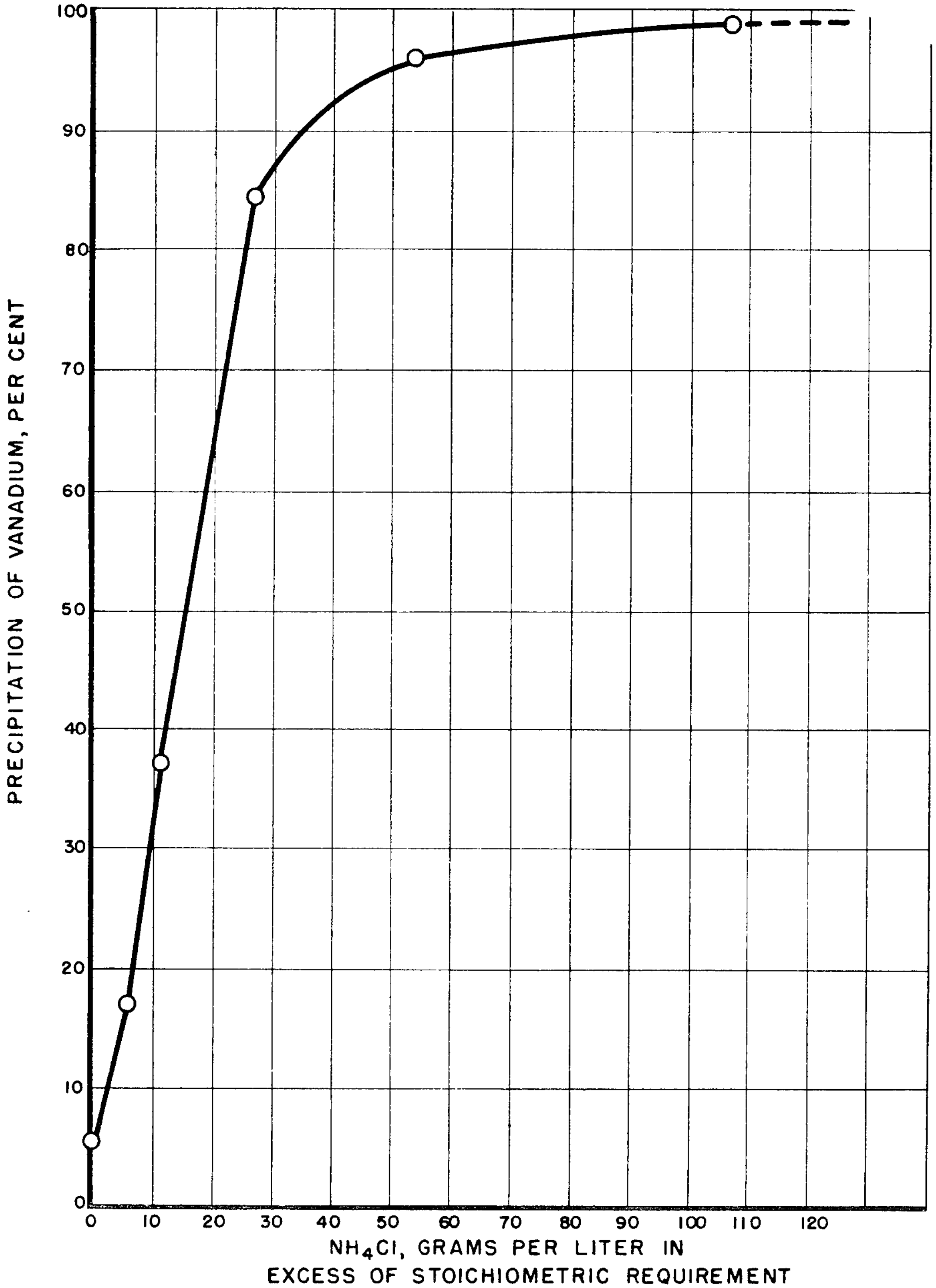

FIGURE 16. EFFECT OF CONCENTRATION OF NH_4Cl ON THE PRECIPITATION OF VANADIUM FROM SODIUM VANADATE SOLUTIONS.

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APPENDIX

TABLE 15. LIST OF REPORTS SUBMITTED UNDER CONTRACT AT-30-1-Gen-258 SINCE THE BEGINNING OF THE PROJECT.

No.	Type of Report	Month	Year	BMI-JDS Report Number	Period Covered
1	Progress	Nov.	1947	1	one month
2	"	Dec.	"	2	"
3	"	Jan.	1948	105	"
4	"	Feb.	"	109	"
5	"	Mar.	"	113	"
6	"	Apr.	"	117	"
7	"	May	"	121	"
8	"	June	"	125	"
9	"	July	"	134	"
10	"	Aug.	"	139	"
11	"	Sept.	"	145	"
12	"	Oct.	"	150	"
13	"	Nov.	"	155	"
14	"	Dec.	"	160	"
15	"	Jan.	1949	167	"
16	"	Feb.	"	174	"
17	"	Mar.	"	180	"
18	"	Apr.	"	186	"
19	"	May	"	192	"
20	Topical	June 15, 1948		128	Nov. 1, 1947 - June 15, 1948
21	Summary	Jan. 15, 1949		162	June 15, 1948 - Jan. 15, 1949
22	Quarterly	Apr. 15, 1949		181	Jan. 15, 1948 - April 15, 1949
23	Final	June 30, 1949		195	Nov. 1, 1947 - June 30, 1949

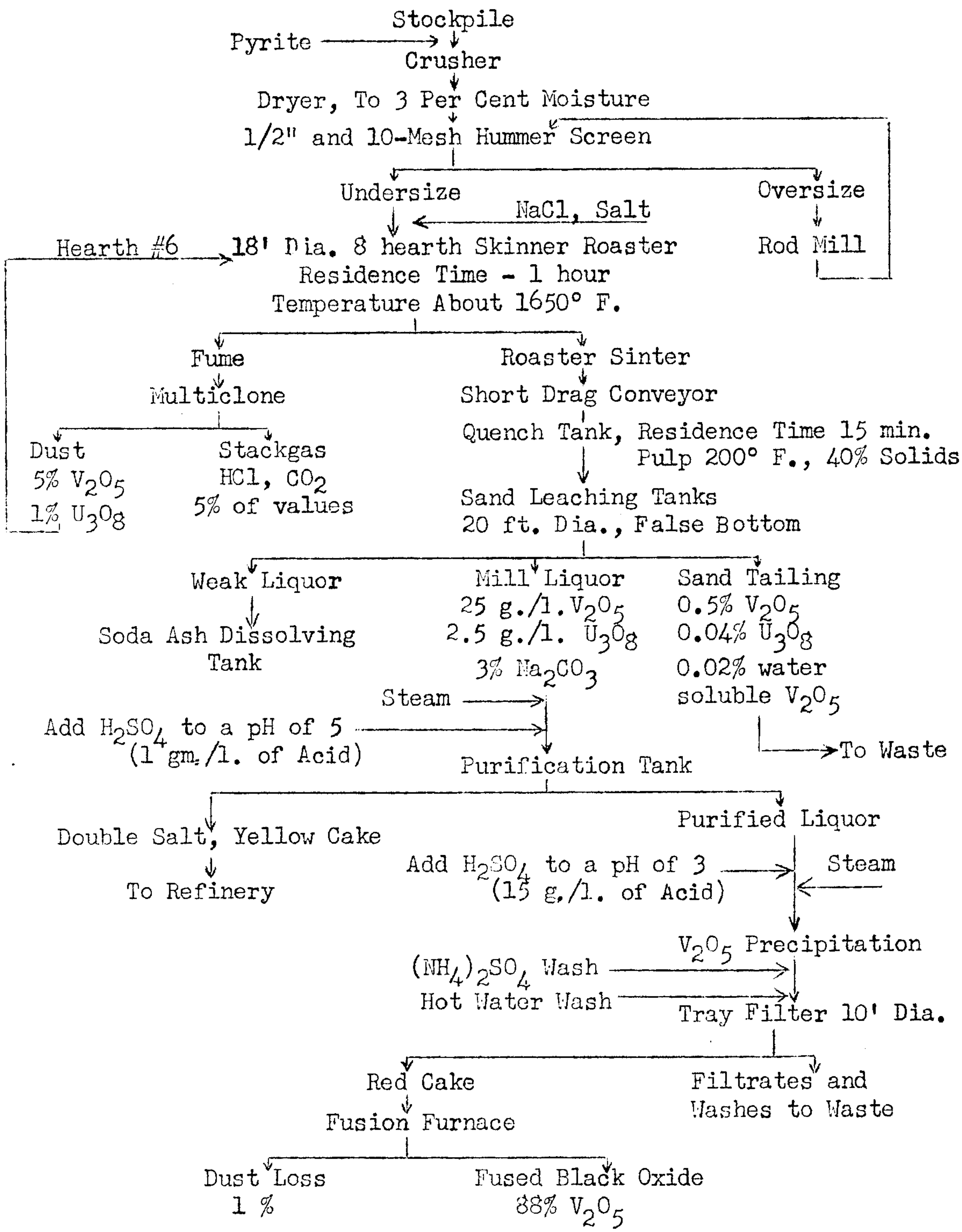

Figure 17. Diagrammatic Flowsheet of Monticello Process.

APPENDIX

TABLE 16. ANALYSES OF ORES TESTED.

Type of Ore	Battelle Number	Source of Ore	Origin	Analyses, Per Cent										
				U	V_2O_5	SiO_2	CaO	Fe_2O_3	Al_2O_3	F_2	MgO	S	Na_2O	K_2O
Normal Carnotite	C-7	Wild Steer Mine	South Side of Paradox Valley, Colorado	0.34	3.40	86.16	0.79	.71	4-6(1)	<.01	1.4	.094	-	-
Med.-Lime Carnotite	C-8	Gyp Valley	Dolores River, San Miguel Co., Colorado	0.57	2.88	78.77	2.54	1.19	4.0	.02	1.4	.034	0.1	1.0
Med.-Lime Carnotite	C-9	Garbutt Group	14 Miles SW of Blanding, Utah	0.14	2.70	79.41	3.80	2.18	-	<.01	1.8	.065	-	-
Roscoelite	C-10	Fall Creek	3 Miles East of Placerville, Colorado	0.052	2.70	82.05	1.70	2.76	-	-	0.6	.054	-	-
Roscoelite	C-11	Dunning Claims	Hermosa Creek, Rico, Colorado	0.075	2.72	82.48	2.60	2.91	-	<.01	0.6	.054	-	-
Slime Concentrate	C-12	Mex. Hat Conc.	Indian Reservation, Mon. #2	0.56	2.12	75.17	2.12	4.65	-	-	-	-	-	-
Low-Lime Carnotite	C-13	Yellow Bird	LaSal Creek Montrose Co., Colorado	0.28	1.89	-	0.06	-	-	-	1.4	.014	-	-
Low-U Carnotite	C-14	Henry Mt.	South Central Utah	0.04	1.61	-	1.67	-	-	-	0.8	.091	-	-
Normal Carnotite	C-15	Ownbey	25 Miles N NW Egnar, Colo.	0.17	1.58	-	0.76	-	-	-	0.4	.045	-	-
Dolomitic Shale	C-16	Bald Eagle	15 Miles East, Slick Rock, Colorado	0.72	2.60	-	17.6	-	-	-	10.5	.052	-	-
3% Lime, Normal Blend	C-19	Blend C	Possible Mill-Feed to Monticello	0.32	2.23	81.1	3.00	-	-	-	-	-	-	-
Normal Carnotite	C-20	Radium 7,(2)	Mickey O'Neill Claims San Miguel Co., Colo.	0.34	2.56	81.3	3.40	2.12	5.1	-	-	<.1	0.24	0.75
High-Lime Ore	C-21	Bald Eagle No.2	15 Miles East, Slick Rock, Colorado	0.17	1.45	-	-	-	-	-	-	-	-	-

(1) Spectrographic

(2) Additional analysis of C-20 include: P_2O_5, 0.03% and TiO_2, 0.12%

TABLE 17. OPTIMUM ROASTING CONDITIONS AND EXTRACTIONS OF ORE TESTED.

Ore	Battelle Number	Optimum Roasting Conditions[1]: Roasting Temp., °F.	Roasting Time, Min.	Salt Added, %	Pyrite Added, %	Maximum Extractions, Per Cent: U	V_2O_5	With V_2O_5 Added[2]: V_2O_5 Added Per Cent	Maximum Extraction, Per Cent: U	V_2O_5[3]	Soda Soluble U.	Classification
Wild Steer	C-7	1520-1560	30-60	10	0	80	65	0.66	89	93	92	Responsive
Gyp Valley	C-8	1380-1470	1	10	0	30[4]	-	8	83	88	92	Mildly Responsive
Garbutt Group	C-9	1650	15	16	0	75	-	-	-	-	-	Responsive
Rico	C-11	1560	40	9	0	70	50	7	93	-	-	Mildly Responsive
Bald Eagle	C-16	390	15	0 or 10	No Effect	62[5]	8	57	60	62	76	Nonresponsive
Blend C	C-19	1560	15	6-10	0	45	-	9	65	87	92	Nonresponsive
Radium 7	C-20	1560	30	10	0	80	-	9	83	85	92	Responsive

(1) Refers to optimum conditions in the range of normal salt roasting. These figures are the results of the standard leach procedure and do not represent soda-soluble uranium. If ores are not roasted, results are given in Table 18 on results of raw ore leaching tests.

(2) Roasting conditions were 1560°F. for 30 minutes, 10 per cent of salt. V_2O_5 was added in a stoichiometric amouht to convert the CaO reported in the ore analyses to $CaO.V_2O_5$.

(3) Per cent of total V_2O_5 in ore plus added V_2O_5.

(4) When 12 per cent of pyrite was added to the roast the uranium extraction was 50 per cent but the solubilization was due to a sulphating action rather than due to salt roasting. An equivalent extraction would be secured by using SO_2 gas.

(5) The extraction of uranium from Bald Eagle Ore C-16 by the normal salt roasting procedure (roast at about 1380°F.) was about 15 per cent.

TABLE 18. RAW ORE LEACHING TESTS

Ore	Uranium Extraction, Per Cent	
	Standard Leach	Special Leach[1]
C-7 Wild Steer	51	ND
C-8 Gyp Valley	82	92
C-9 Garbutt	74	99
C-16 Bald Eagle	62	100
C-20 Radium 7	71	93

(1) Minus 150-mesh raw ores leached for one hour; other leaching conditions were standard.